PB83-262915

Rapid Screening Technique for Detection of Asbestos Fibers in Water Samples

Ontario Research Foundation, Mississauga

Prepared for

Environmental Research Lab., Athens, GA

Sep 83

U.S. Department of Commerce
National Technical Information Service
NTIS

EPA-600/4-83-041
September 1983

PB83-262915

RAPID SCREENING TECHNIQUE FOR DETECTION OF ASBESTOS FIBERS IN WATER SAMPLES

by

E.J. Chatfield and P. Riis
Electron Optical Laboratory
Department of Applied Physics
Ontario Research Foundation
Sheridan Park Research Community
Mississauga, Ontario, Canada L5K 1B3

Contract 68-03-2717

Project Officer

J. MacArthur Long
Analytical Chemistry Branch
Environmental Research Laboratory
Athens, Georgia
30613

ENVIRONMENTAL RESEARCH LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
U.S. ENVIRONMENTAL PROTECTION AGENCY
ATHENS, GEORGIA 30613

REPRODUCED BY
NATIONAL TECHNICAL
INFORMATION SERVICE
U.S. DEPARTMENT OF COMMERCE
SPRINGFIELD, VA. 22161

TECHNICAL REPORT DATA
(Please read Instructions on the reverse before completing)

1. REPORT NO.	2.	3. RECIPIENT'S ACCESSION NO.
EPA-600/4-83-041		PB83-262915

4. TITLE AND SUBTITLE	5. REPORT DATE
Rapid Screening Technique for Detection of Asbestos Fibers in Water Samples	September 1983
	6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S)	8. PERFORMING ORGANIZATION REPORT NO.
E.J. Chatfield and P. Riis	
9. PERFORMING ORGANIZATION NAME AND ADDRESS	10. PROGRAM ELEMENT NO.
Department of Applied Physics Ontario Research Foundation Sheridan Park Research Community Mississauga, Ontario, Canada L5K 1B3	CBNC1A
	11. CONTRACT/GRANT NO.
	68-03-2717
12. SPONSORING AGENCY NAME AND ADDRESS	13. TYPE OF REPORT AND PERIOD COVERED
Environmental Research Laboratory--Athens GA Office of Research and Development U.S. Environmental Protection Agency Athens, Georgia 30613	Final, 10/78-9/81
	14. SPONSORING AGENCY CODE
	EPA/600/01

15. SUPPLEMENTARY NOTES

16. ABSTRACT

A rapid screening method is presented that will allow samples containing less than a pre-defined concentration of asbestos fibers to be rejected from further analysis, allowing more detailed transmission electron microscopy characterization to be confined to those samples that have high fiber concentrations. Alignment of asbestos fibers in magnetic fields, combined with measurements of the scattered light from the aligned dispersions, was investigated. A fixed-fiber alignment method and a dynamic method of fiber measurement were studied. The dynamic fiber method proved to be the more sensitive method. Detection limits of 0.5 million fibers per liter (MFL) and 5 MFL were achieved for crocidolite and chrysotile, respectively. These detection limits were achieved directly from the water sample without any preconcentration steps. The scattered light measurement techniques were applied to the determination of the fiber concentrations in drinking water samples from three sources, and the results were consistent with those obtained independently by transmission electron microscopy.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group

18. DISTRIBUTION STATEMENT	19. SECURITY CLASS *(This Report)*	21. NO. OF PAGES
RELEASE TO PUBLIC	UNCLASSIFIED	86
	20. SECURITY CLASS *(This page)*	22. PRICE
	UNCLASSIFIED	

EPA Form 2220-1 (9-73)

NOTICE

THIS DOCUMENT HAS BEEN REPRODUCED FROM THE BEST COPY FURNISHED US BY THE SPONSORING AGENCY. ALTHOUGH IT IS RECOGNIZED THAT CERTAIN PORTIONS ARE ILLEGIBLE, IT IS BEING RELEASED IN THE INTEREST OF MAKING AVAILABLE AS MUCH INFORMATION AS POSSIBLE.

DISCLAIMER

The information in this document has been funded wholly or in part by the United States Environmental Protection Agency under Contract No. 68-03-2717 to Ontario Research Foundation. It has been subject to the Agency's peer and administrative review, and it has been approved for publication as an EPA document. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

FOREWORD

Nearly every phase of environmental protection depends on a capability to identify and measure specific pollutants in the environment. As part of this Laboratory's research on the occurrence, movement, transformation, impact, and control of environmental contaminants, the Analytical Chemistry Branch develops and assesses new techniques for identifying and measuring chemical constituents of water and soil.

A 3-year study was conducted to develop improvements in the analytical method for determination of asbestos fiber concentrations in water samples. The research produced an improved sample preparation and analysis methodology, a rapid screening technique to reduce analysis cost, and a new reference analytical methodology for asbestos in water. The analytical method for determining asbestos fibers in water is perceived as representing the current state-of-the-art.

William T. Donaldson
Acting Director
Environmental Research Laboratory
Athens, Georgia

PREFACE

Analyses of water samples for the presence of asbestos fibers are made by transmission electron microscopy (TEM), using selected area electron diffraction and energy dispersive X-ray analysis to identify each individual fiber. The fiber identification and counting procedure is labor-intensive, and the resulting high analytical costs have limited the extent to which water supplies can be monitored routinely for asbestos fibers. A rapid method is required which will allow samples containing lower than a pre-defined concentration of asbestos fibers to be rejected from further analysis, allowing more detailed TEM characterization to be confined to those samples which have high fiber concentrations. A rapid method is also required for routine monitoring of fiber concentrations in water sources where asbestos fibers are known to be present at concentrations of concern. Measurement of the light scattered by magnetically aligned fibers was investigated as a rapid screening method.

ABSTRACT

When placed in a strong magnetic field, asbestos fibers in liquid suspension adopt preferred alignment directions relative to the field direction. Fibers may align parallel to, normal to, or at a constant angle to the magnetic field, depending on the mineralogical variety of fiber. Light is scattered more strongly in directions normal to the length of the fiber, and thus observation of the scattered light pattern from an aligned fiber dispersion can yield a measurement of fiber concentration. The application of this method as a means for rapid measurement of asbestos fiber concentration in water samples has been investigated.

A fixed fiber alignment method has been studied in which an aqueous fiber dispersion is filtered through a membrane filter located in a strong magnetic field. This results in a filter on which the asbestos fibers are permanently aligned in preferred directions. When the filter is exposed to solvent vapor, the structure collapses and the filter becomes transparent. Rotation of the filter in a collimated beam of light yields maxima in the intensity of the scattered light; the positions of these maxima are related to the alignment direction of the fibers.

A dynamic fiber method of measurement has also been investigated in which the behavior of aqueous asbestos fiber dispersions in a rotating magnetic field is observed. A spectrophotometer cell which contains the fiber dispersion is placed between the poles of a rotating magnet, and is illuminated by a collimated beam of light. The fibers rotate in synchronism with the magnetic field, and maxima in the intensity of the forward scattered light are observed. Since light is scattered more strongly in directions normal to the lengths of fibers, a maximum in intensity of the scattered light occurs for every 180° of fiber rotation. When the scattered light is monitored and the intensity displayed as a function of magnet position, the areas under the peaks are proportional to the fiber concentration.

It was found, using the fixed fiber alignment method, that the lowest detection level was limited by the residual structure in the collapsed membrane filter. For UICC crocidolite and UICC amosite, the detection level was about 0.1 ng/mm^2, and for chrysotile about 1 ng/mm^2. If 25 mm diameter filters were used, these detection levels correspond to filter loadings of about 20 ng and 200 ng respectively. The dynamic fiber method achieved much lower detection limits of 180 ng/L and 30 ng/L for crocidolite and chrysotile respectively. These detection limits apply to the 5 mL volume of aqueous fiber dispersion in the spectrophotometer cell, and correspond to detection of 0.9 ng of crocidolite and 0.15 ng of chrysotile. It was found that the required detection limits of 0.2 million fibers per liter (MFL) or 1 ng/L can be achieved with the incor-

poration of a selective fiber concentration technique. A limited study was made of the high gradient magnetic separation technique for amphibole fibers. A new method was also devised for separation of chrysotile fibers by selective adhesion to organic materials.

The developed scattered light measurement techniques were applied to determination of the fiber concentrations in drinking water samples from three sources, and the results were consistent with those obtained independently by transmission electron microscopy.

Mineral species other than the asbestos varieties were examined with the dynamic fiber method in order to determine possible interferences. The results indicated that non-fibrous material which rotates with the magnetic field yields broad scattered light maxima at about 45° and 225° to the magnetic field direction. Qualitative measurements showed that many other fibrous mineral species yielded alignment modes similar to those obtained with the asbestos varieties.

The analytical time required for a single measurement using the current instrumentation is less than 10 minutes; labor requirements for sample preparation are variable depending on the fiber concentration steps incorporated, but these need not exceed 1 man-hour per sample.

CONTENTS

Foreword iii
Preface iv
Abstract v
Figures ix
Tables xii
Acknowledgment xiii

1. INTRODUCTION 1

1.1 Applications of a Rapid Screening Technique 1
1.2 Required Features of a Rapid Screening Technique 1
1.3 Possible Technical Approaches 2
1.3.1 Chemical Analysis Methods 2
1.3.2 X-ray Diffraction Methods 3
1.3 3 Infrared Spectroscopy 3
1.3.4 Two Phase Liquid Separation 3
1.3.5 Single-Particle Scattered Light Measurement Technique 4
1.3.6 Measurement of Scattered Light from Magnetically Aligned Fibers 4
1.4 Summary of Available Techniques 4

2. CONCLUSIONS AND RECOMMENDATIONS 6

3. OBSERVATION OF MAGNETICALLY-ALIGNED FIBER SAMPLES 8

3.1 Types of Fiber Alignment 9
3.2 Observation of Alignment Effects by Light Scattering Techniques 10

4. FIXED FIBER ALIGNMENT TECHNIQUE 13

4.1 Equipment Design 13
4.2 Sample Preparation 15
4.2.1 Filtration of Aqueous Fiber Dispersions 15
4.2.2 Clearing of Membrane Filters 17
4.3 Measurements and Results 21
4.3.1 Measurement of Detection Levels for Asbestos Fibers Dispersed in Double-Distilled Water 21
4.3.2 Effects of Non-Fibrous Particulate 26
4.4 Magnetic Field Requirements for Fiber Alignment 27
4.5 Signal Enhancement Techniques for Improvement of Detection Levels 28
4.5.1 Complete Dissolution of Filter Medium 28

4.5.2 Electronic Noise Reduction 28
4.5.3 Use of Reflective Scattering Techniques 28
4.5.4 Radiofrequency Plasma Etching of Filters 29
4.5.5 Shadowing of Particulate by Vacuum Deposition of Opaque Films 30
4.6 Evaluation of the Fixed Fiber Alignment Technique 31

5. DYNAMIC FIBER TECHNIQUE 33
5.1 Equipment Design 33
5.2 Sample Preparation 37
5.3 Measurements and Results 37
5.3.1 Measurement of Blank Samples 38
5.3.2 Measurement of Detection Levels for Asbestos Fibers Dispersed in Double-Distilled Water 40
5.3.3 Effects of Non-Fibrous Particulate 43
5.4 Evaluation of the Dynamic Fiber Technique 44

6. ALIGNMENT MODES OF SELECTED MINERAL SPECIES IN MAGNETIC FIELDS . 45

7. METHODS FOR CONCENTRATION OF FIBERS 59
7.1 Non-Specific Fiber Concentration 59
7.2 Removal of Organic Particles 59
7.3 Specific Concentration of Chrysotile 59
7.4 Specific Concentration of Amphiboles 62

8. EVALUATION OF THE RAPID SCREENING TECHNIQUE: APPLICATION TO MUNICIPAL DRINKING WATER SAMPLES 66

REFERENCES 69

FIGURES

Number		Page
1	Alignment modes of asbestos fibers in magnetic fields	8
2	Phase contrast optical micrographs	9
3	Scattered light distributions	11
4	Schematic of system used for the analysis of light scattered from aligned asbestos fibers	13
5	System for scattered light measurements of fixed alignment samples	14
6	Sample turntable and photomultiplier	15
7	Filtration assembly located between poles of an electromagnet .	16
8	Equipment used to collapse membrane filters	17
9	UICC Crocidolite: Scattered light profile obtained from a filter loading of 15 ng/mm^2	22
10	UICC Amosite: Scattered light profile obtained from a filter loading of 16 ng/mm^2	22
11	Union Carbide Chrysotile: Scattered light profile obtained from a filter loading of 12 ng/mm^2	22
12	UICC Crocidolite: Scattered light profile obtained from a filter loading of 0.4 ng/mm^2	23
13	UICC Amosite: Scattered light profile obtained from a filter loading of 0.2 ng/mm^2	23
14	Union Carbide Chrysotile: Scattered light profile obtained from a filter loading of 0.6 ng/mm^2	23
15	UICC Crocidolite: Area of P-fiber peak as a function of mass and fiber concentration on filter	24

16 UICC Amosite: Area of P-fiber peak as a function of mass and fiber concentration on filter 24

17 UICC Amosite: Area of N-fiber peak as a function of mass and fiber concentration on filter 25

18 Union Carbide Chrysotile: Area of peak as a function of mass and fiber concentration on filter 25

19 Scattered light profile showing peaks from amosite in municipal drinking water 26

20 Union Carbide Chrysotile: Variation of peak area with magnetic field strength 27

21 Schematic of equipment used for analysis of light scattered from magnetically-aligned fibers in liquid suspension 34

22 Equipment for measurement of scattered light intensities from fibers rotating in liquid suspensions 35

23 Rotating magnet and detection optics of dynamic fiber system .. 35

24 Position encoder located on magnet periphery used to communicate magnet position to the computer 36

25 Sample loading mechanism 37

26 UICC Crocidolite: Dynamic scattered light profile 39

27 UICC Amosite: Dynamic scattered light profile 39

28 Union Carbide Chrysotile: Dynamic scattered light profile 39

29 UICC Crocidolite: Variation of scattered light profile with fiber concentration 41

30 Union Carbide Chrysotile: Variation of scattered light profile with fiber concentration 41

31 UICC Crocidolite: Area of P-fiber peak as a function of mass and fiber concentration 42

32 Union Carbide Chrysotile: Area of peak as a function of mass and fiber concentration 42

33 Scattered light profile of borosilicate glass particle suspension 43

34 - 81 Scattered light profiles (selected minerals) 46-57

82 High gradient magnetic separator 63

83 The effect of magnetic field strength on retention of amosite fibers 64

84 Magnetic separator retention efficiency for UICC amosite 64

85 Scattered light profile of water sample from Beaver Bay, Minnesota, before and after subtraction of general particle peak 67

86 Scattered light profile of water sample from Sherbrooke, Quebec, before and after subtraction of general particle peak 67

87 Scattered light profile of water sample from Mississauga, Ontario, before and after subtraction of general particle peak 68

TABLES

Number		Page
1	Measurement of Scattered Light from Sample Preparation Media	20
2	Measurement of Scattered Light from Samples Prepared by the Dichloroethane-AIA Technique	20
3	The Effect of R.F. Plasma Etching on Aligned Crocidolite Fiber Samples	30
4	Improvements in Peak/Background Ratio Produced by Gold Coating	31
5	Summary of Fiber Removal from Water Samples	61

ACKNOWLEDGMENTS

The authors wish to acknowledge the invaluable assistance of Mr. F. Bottone, Mr. J. Hackett and Mr. T. Scott, who were responsible for much of the instrumental and software development. They also wish to express their appreciation to Mr. L. Doehler and Mrs. A. Liebert for their patience during many hours of sample preparation and TEM evaluation. The authors also wish to thank Dr. G. Plant of the Geological Survey of Canada, and Drs. F.J. Wicks and R.I. Gait of the Royal Ontario Museum for helpful discussions and for supply of the many mineral samples. The authors especially want to thank Mrs. M. Cochrane, Mrs. M.J. Dillon and Mrs. S. Newman for their outstanding effort in preparing this manuscript.

SECTION 1

INTRODUCTION

1.1 APPLICATIONS OF A RAPID SCREENING TECHNIQUE

Current methods for measurement of the concentration of asbestos fibers in water samples[1] require a minimum of approximately five hours of labor for each sample. This procedure is time-consuming and expensive in both labor and equipment, requiring about three hours of fiber identification and counting by a skilled operator using an analytical electron microscope. A rapid analytical method is required for the following two applications:

(a) to select for detailed electron microscope analysis only those samples which have fiber concentrations exceeding some specified value, and;

(b) to allow frequent and economically viable monitoring of water sources in which the fiber content has already been adequately characterized.

1.2 REQUIRED FEATURES OF A RAPID SCREENING TECHNIQUE

If a rapid screening method is to be useful, the economic advantages over conventional methods based on electron microscopy must be worthwhile. In particular, the equipment required should be significantly less expensive than the analytical electron microscope, and the instrument time required for each analysis should be short. Elimination of the requirement for highly qualified and skilled personnel to conduct the analysis would also be very desirable. In assessing the suitability of the available methods, sample preparation labor and the time required for the actual measurement must be considered carefully. The features of a rapid screening technique should include:

(a) substantially less labor expenditure than that required for conventional electron microscopy techniques;

(b) as a consequence of (a), the technique should not rely on manual fiber counting techniques, either by electron microscopy or light microscopy;

(c) routine analysis should be possible without the requirement for a high degree of skill;

(d) it should not require expensive equipment;

(e) it must be sufficiently sensitive for detection of 0.2 million fibers per liter (MFL) or 1 nanogram per liter (ng/L);

(f) it should be able to distinguish between chrysotile and amphibole asbestos fibers.

1.3 POSSIBLE TECHNICAL APPROACHES

If electron microscopy is excluded, the possibilities for a rapid screening technique fall into three categories: those which consist of a simple chemical measurement, and other more sophisticated approaches which selectively detect either the mineral species or the actual mineral fibers present. Certainly, a rapid screening technique cannot incorporate manual fiber counting in any form.

1.3.1 Chemical Analysis Methods

Chemical methods are based on the detection of one or more of the constituent elements of asbestos. The element or elements are usually selected for analysis on the basis of instrumental sensitivity and the ease of analytical technique. Unfortunately, the constituent elements of the asbestos minerals are not specific. All of the elements concerned are present in many other minerals and compounds generally present in air, water, and soil at concentrations which are orders of magnitude higher than the level of asbestos. Methods based on analysis of specific elements can therefore be used only when it is known that the samples contain considerable amounts of asbestos relative to other species which might interfere. This may be the case for some samples associated with asbestos-processing industries, but in the general case little is known about the particular sample.

Atomic absorption, flame spectroscopy, emission spectroscopy and X-ray fluorescence have been considered for analysis of environmental samples for asbestos.[2] For measurement of magnesium, the lowest detection level of 100 ng is achieved by atomic absorption. This would still require concentration of asbestos from about 400 liters of water in order to achieve a detection limit of 1 ng/liter for chrysotile in water.

Moreover, in a recent study of the chrysotile concentrations in some wine and water samples,[3] it was found that the insoluble magnesium concentrations were of the order of micrograms/liter, compared with the nanogram/liter levels of asbestos reported in similar samples by electron microscope fiber counting. This indicates that the chrysotile fibers may contain only 0.1% of the total insoluble magnesium in a typical water sample, an observation which invalidates the use of simple chemical methods for this type of sample.

In summary, the only justifiable application of the simple chemical measurement is the case where the particular variety of asbestos is known to be the only species present which contains the element being analyzed. Furthermore, compositional variations within the same species of asbestos demand that a calibration be performed using asbestos from the *same* source.

1.3.2 X-ray Diffraction Methods

X-ray diffraction (XRD) is capable of specific detection of individual mineral species. Quantitative determination by X-ray diffraction requires the use of a series of known standards; the intensities of a particular characteristic reflection are determined for the unknown and for the standards. From the ratio of the intensities, the unknown quantity of asbestos in the samples can be obtained.[4] The best minimum detectable weight is reported to be approximately 1 microgram (µg), and the asbestos must comprise more than about 1% of the total sample.[2] For reliable determinations, 15 to 20% asbestos may be required.[5,6] Grinding of a sample during preparation has been shown to affect significantly the sensitivity of the measurements by X-ray diffraction.[7,8]

A feasibility study has been reported[9] in which the fibers were aligned electrostatically before the X-ray measurements were made. In this way the detection level of the technique for chrysotile asbestos was improved to about 0.2 µg, but it was estimated that this would be degraded to about 0.4 µg if the asbestos were present in a mixture of other materials.

Thus the detection level of X-ray diffraction methods is inadequate for application as a screening technique for unknown samples.

1.3.3 Infrared Spectroscopy

The detection level of the infrared spectroscopy technique is only about 20 µg, and the method is subject to many interferences.[2,10] Accordingly, it is not appropriate as a screening method for asbestos in unknown environmental water samples.

1.3.4 Two Phase Liquid Separation

A technique based on two phase liquid separation (TPLS) has recently been described[11] in which selective extraction of chrysotile from water into an organic solvent phase is promoted by an anionic surfactant. Over most of the pH range chrysotile has a positive zeta potential, in contrast to the negative zeta potentials of most other waterborne particulate species. The surfactant consequently reacts selectively with the chrysotile, and the fibers become hydrophobic. The aqueous phase is then shaken with iso-octane until an emulsion is formed. The emulsion

is salted out with sodium chloride solution, and the chrysotile is found in the iso-octane.

Several successive extractions are necessary to achieve a recovery of about 75%. The iso-octane is then filtered, using a Nuclepore® polycarbonate filter. The filter is carbon coated and fibers on its surface are counted in reflected light. The sensitivity for chrysotile was reported as about 1 ng/L. Unfortunately, the surface properties of the amphiboles are similar to those of many other particulate species; consequently it is doubtful whether any useful separation of amphibole fibers could be achieved using this technique.

1.3.5 Single-Particle Scattered Light Measurement Technique

A method developed by Diehl et al[12] is based on light scattering using a focused laser beam, and observation of the light pulse from a single particle. Use of several detectors which view the light pulse from different directions permits some degree of particle shape discrimination. However, the technique requires a complete initial characterization of the water source by electron microscopy for calibration of the output. Any fluctuation in the relative proportions of the different types of particulate may lead to an erroneous result. The possibility of error, and the requirement for prior electron microscopic characterization of the sample, make this method unsuitable as a rapid screening technique.

1.3.6 Measurement of Scattered Light from Magnetically Aligned Fibers

Preliminary experiments described by Timbrell[13] have shown that asbestos fibers adopt preferred alignment directions when suspended in a magnetic field. Using relatively simple equipment, the combination of this effect with scattered light measurements was reported to be capable of detecting a few nanograms of fibers. Moreover, since the technique is based on light scattering, it is not limited to measurement of only those fibers which can be resolved in the optical microscope. Fibers which do not align in the magnetic field, and randomly shaped particles, do not contribute to the measurement. Some degree of discrimination between the fiber types is possible because their alignment modes are different.

1.4 SUMMARY OF AVAILABLE TECHNIQUES

Techniques such as chemical analysis, X-ray diffraction, and infrared spectroscopy are unsuitable as the basis of a rapid screening technique either on the grounds of inadequate detection level or lack of specificity. Although detection levels could possibly be improved by some pre-concentration step, low specificity would lead to an unacceptable number of false positive results.

A screening technique should preferably be capable of detection of asbestos *fibers*, and this is why the previous work in this area has concentrated either on some unique property of asbestos, as in the TPLS method, or on specific methods for detecting elongated particles. Application of the TPLS method appears to be limited to chrysotile, and, in order to achieve the detection levels required, the sample analysis is based on manual fiber counting using an optical microscope. The single-particle scattered light technique would be capable of significant further development, but it is not capable of species discrimination and all elongated particles are counted regardless of composition.

The magnetic alignment approach has many of the features required for a rapid screening technique. It appears to be more sensitive than any other technique considered, apart from the single-particle scattered light method. It has also been demonstrated that it is sensitive only to fibers, with a further restriction that they must adopt some preferred alignment in a magnetic field. The alignment mode is also species-dependent to some limited extent, leading to the possibility of discrimination between different asbestos varieties. For these reasons the magnetic alignment technique was selected for further development.

SECTION 2

CONCLUSIONS AND RECOMMENDATIONS

The measurement of scattered light from magnetically aligned asbestos fibers has been demonstrated as a suitable method for detection of asbestos fibers in water samples. Two techniques were investigated.

The technique based on filtration of fiber dispersions in a magnetic field was found to have an inadequate detection level, primarily limited by the residual structure of the membrane filter. The detection limit for fiber size distributions similar to those found in water samples was about 10^2 fibers/mm^2 for UICC crocidolite and about 10^5 fibers/mm^2 for Union Carbide chrysotile. In order to detect a concentration of 0.2 MFL of chrysotile, filtration of about 100L of water through an active filter area of 200 mm^2 would be required. Signal enhancement techniques such as RF plasma etching of the filter and shadowing of the particulate by evaporated metal films failed to improve the detection limits significantly.

The liquid suspension technique was shown to have detection limits of 0.5 MFL for UICC crocidolite and 5 MFL for Union Carbide chrysotile. These detection limits can be achieved directly from the water sample without any pre-concentration steps.

In the investigation of light scattering from liquid suspensions, it was found that particles of random shape which rotate with the magnetic field produce a broad maximum of scattered light intensity corresponding to alignment at an angle of 45° to the magnetic field direction. This effect was observed, for example, with borosilicate glass fragments, and is in contrast with the simple increase in constant scattering obtained from particulate which is unaffected by the magnetic field. In general, however, the presence of other particulate degrades the detection limit, and therefore specific fiber separation techniques were investigated. HGMS (high gradient magnetic separation) was successful in extracting UICC crocidolite and amosite, having a 95% numerical collection efficiency for dispersions of amosite. Because they are not strongly magnetic, fibers of chrysotile were not retained by the magnetic separator. Therefore HGMS is a useful technique for separating chrysotile asbestos from amphibole asbestoses which contain high concentrations of iron.

A new separation technique which is based on scavenging of fibers by organic materials was successful for specific separation of chrysotile. The same technique also appears to allow concentration of crocidolite and amosite fibers, but it is not yet established if the separation is specific. The

recovery of separated chrysotile was between 87% and 100% for standard dispersions, falling to about 45% in the case of drinking water samples.

Three municipal water supplies were analyzed directly by the rotating fiber method. The particulate of random shapes yielded prominent, broad peaks at 45° and 225°, and it was necessary to perform profile subtractions in order to extract the signal originating from the fibers present. The residual peaks after this procedure agreed with the known asbestos fiber levels. For a water sample from Beaver Bay, Minnesota, the 45° component was subtracted and this resulted in residual peaks at 0° and 180°, and at 90° and 270°. This agrees with the known asbestos content of the water: cummingtonite is known to align parallel and grunerite normal to the magnetic field direction. It was possible to measure directly the chrysotile fiber concentration in a municipal water which has a concentration of 40 MFL. Application of the fiber separation technique to the same sample yielded a concentrated suspension for analysis which contained only chrysotile.

With pre-concentration of the fibers from water samples, the rotating magnet method is capable of detecting concentrations of 0.2 MFL or 1 ng/L of asbestos fibers. Development of computer profile subtraction techniques will permit the separation of the components corresponding to mineral fibers from the total scattered light profile. This will reduce the amount of sample preparation required for separation and pre-concentration. Variation of the rotation rate and strength of the magnetic field may provide additional information by which particle species may be differentiated. In routine use, it is estimated that water samples could be analyzed directly in five to ten minutes, while samples requiring separation or pre-concentration would require less than one man-hour for preparation and analysis.

The alignment modes of a number of fibrous mineral species in a magnetic field were investigated qualitatively. Some yielded broad scattered light profiles similar to those from chrysotile, while others displayed sharper peaks from fibers aligned in directions parallel or normal to the magnetic field. If the primary purpose is the detection of "asbestos" then there is some potential for interference by fibrous species other than those normally considered to be asbestos. Assuming that the purpose of the technique is to determine if any fibrous mineral species are present, then it is highly successful, extremely sensitive, and allows for some discrimination between mineralogical species.

Assuming some pre-concentration of the sample, the magnetic alignment technique has the required detection level and sensitivity for measurement of fiber concentrations in water. It is capable of significant further development, particularly for the determination of fiber dimensions. More extensive fiber characterization could also be achieved on the basis of iron content and alignment mode. Further research is also required to optimize the specific fiber separation techniques.

SECTION 3

OBSERVATION OF MAGNETICALLY-ALIGNED FIBER SAMPLES

3.1 TYPES OF FIBER ALIGNMENT

When asbestos fibers are suspended in a liquid and placed in a strong magnetic field, about 1.0 tesla (T), they become aligned in one of the three possible modes illustrated in Figure 1. Depending on the type of fibers, and in some cases their origin, they may align parallel to the field direction (P-type), normal to the field (N-type), or transversely to the field at a constant angle (T-type). Optical microscope slides can be prepared on which asbestos fibers are permanently fixed in their preferred alignments relative to a magnetic field. The suspension of fibers is initially prepared either in an aqueous agar solution or in a dilute solution of nitrocellulose in n-pentyl acetate. A drop of the suspension is placed on a microscope slide, which is then placed between the poles of a magnet and in a horizontal position such that the field direction is in the plane of the slide. As the suspension medium evaporates and solidifies, the fibers contact the surface of the microscope slide, thus placing an additional constraint on their orientations. Once the suspension medium has dried, the microscope slide may be viewed in optical phase contrast illumination to determine the mode of alignment for the particular species of fiber.

Figure 1. Alignment modes of asbestos fibers in magnetic fields. (After Timbrell, 1975)

Some examples of samples prepared by this procedure are shown in Figure 2. Figure 2a shows a phase contrast optical micrograph of an unaligned dispersion of UICC (Union Internationale Contre le Cancer) crocidolite; this can be compared with Figure 2b which shows a similar

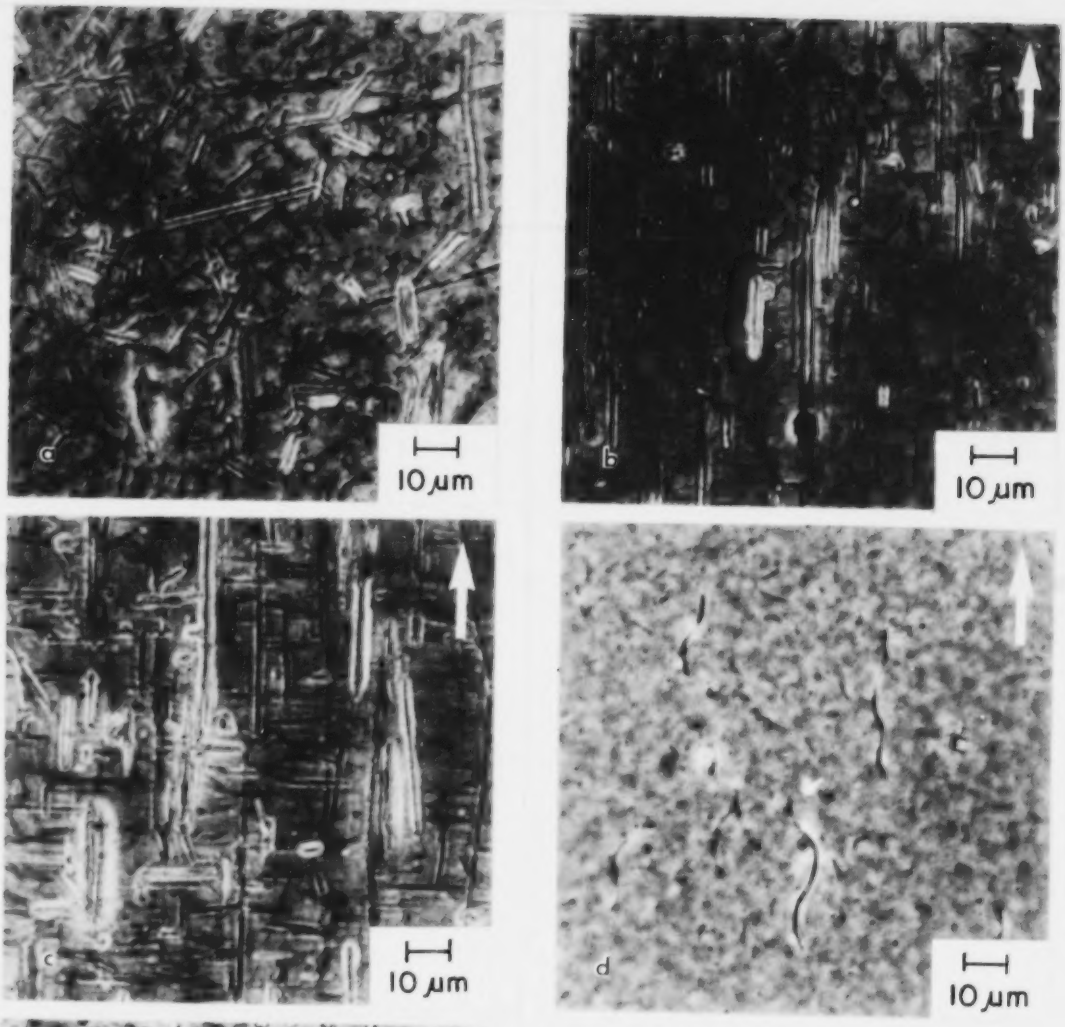

Figure 2.

Phase contrast optical micrographs of:

a) unaligned UICC crocidolite;

b) aligned UICC crocidolite;

c) aligned UICC amosite;

d) aligned UICC Canadian chrysotile;

e) aligned New Zealand cummingtonite.

(The magnetic field direction is indicated on the figures).

sample prepared in a magnetic field of 1.0 T. In the case of crocidolite, the majority of the fibers are aligned parallel to the magnetic field and a smaller number are aligned in directions perpendicular to the field. Figure 2c shows a phase contrast optical micrograph of an aligned UICC amosite dispersion, and illustrates that for this mineral there are large numbers of both N-type fibers and P-type fibers. Figure 2d shows the alignment effect observed with UICC Canadian chrysotile. Although the fibers are P-type, their curvatures do not permit the precise alignment which is obtained with crocidolite and amosite. Figure 2e shows an aligned sample of a variety of cummingtonite from New Zealand, which contains T-type fibers with their alignment directions symmetrically disposed at a constant angle about the field direction.

It is reported that the alignment of asbestos fibers in a magnetic field occurs because they are either paramagnetic or weakly ferromagnetic, and that chrysotile behaves in this way because of the presence of particles of magnetite in the fibers.[13] The P-fiber alignment mode is a consequence of the direction of maximum magnetic susceptibility being parallel to the length of the fiber; for N-fibers it is normal to the length of the fibers, and for T-fibers it is at some angle to the fiber length.

Unpublished work by Cressey and Whittaker[14] on amphiboles indicates that the existence of the alignment effect is probably associated with the fiber structure itself, rather than being a consequence of any inclusions of strongly magnetic materials. In a study of the crystallographic orientations of aligned amphibole fibers by selected area electron diffraction, they found that N-type UICC amosite fibers were aligned with the crystal y-axis oriented within ±20° of the field direction. This is explained if the axis of greatest magnetic susceptibility is parallel to the y-axis and further supports the idea that the alignment effect is due to the crystallographic structure of the fiber. Angular restrictions about the z-axis of P-type fibers were also found, but were of a much broader range. No precise explanation for the different alignment behaviors of P-type and N-type fibers has so far been reported. In the case of chrysotile, although no systematic study has been made, the alignment effect can still be demonstrated for varieties of chrysotile which have very low iron concentrations.

3.2 OBSERVATION OF ALIGNMENT EFFECTS BY LIGHT SCATTERING TECHNIQUES

When a beam of light is used to illuminate a fiber, light is scattered preferentially in directions perpendicular to the length of the fiber. For a distribution of randomly-oriented fibers this results in random light scattering in all directions. To observe the effect of fiber alignment on the light scattering behavior, a microscope slide prepared as described in 3.1 is placed in the path of a collimated beam of light projecting on to a white opaque screen. The image obtained is the scattered light distribution of the sample. Examples are shown in Figure 3. These figures were obtained by photographing the distribution projected on the screen.

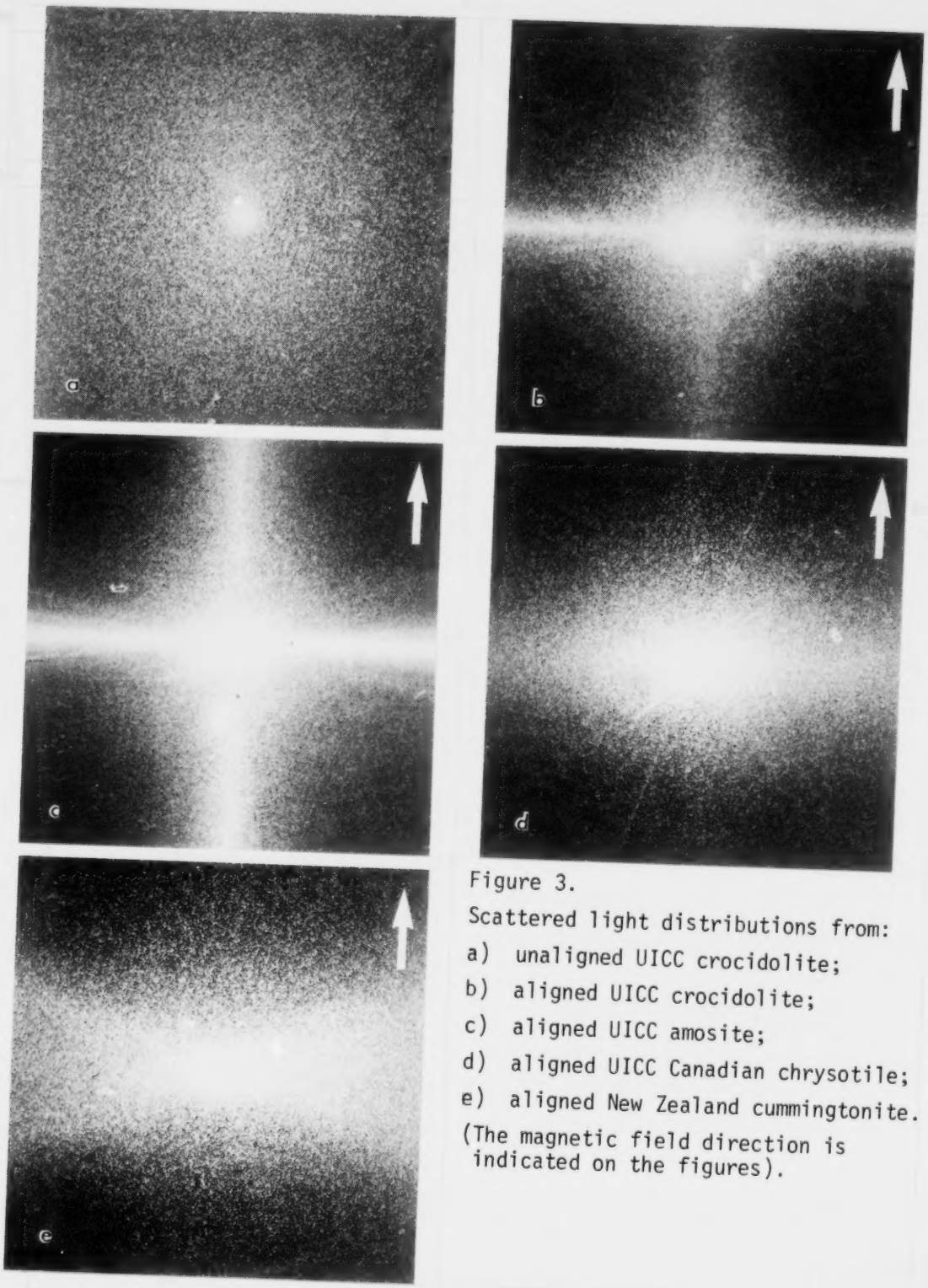

Figure 3.

Scattered light distributions from:

a) unaligned UICC crocidolite;

b) aligned UICC crocidolite;

c) aligned UICC amosite;

d) aligned UICC Canadian chrysotile;

e) aligned New Zealand cummingtonite.

(The magnetic field direction is indicated on the figures).

An unaligned sample of UICC crocidolite yields the circularly symmetrical pattern in Figure 3a. When fibers have been aligned in a magnetic field, the scattered light distributions from individual fibers are also aligned, resulting in a maximum in the scattered light intensity in directions perpendicular to the lengths of the fibers. This is illustrated in Figures 3b to 3e for magnetically-aligned distributions of crocidolite, amosite, chrysotile and New Zealand cummingtonite respectively. Most of the crocidolite fibers are aligned parallel to the magnetic field, resulting in sharp scattered light maxima perpendicular to the field direction, but small N-fiber maxima are also visible. Amosite contains large quantities of both P-type and N-type fibers, resulting in scattered light maxima both perpendicular and parallel to the magnetic field. Chrysotile fibers are aligned parallel to the field direction, but because the fibers are often curved, there is incomplete alignment and the maximum in the scattered intensity is much broader. New Zealand cummingtonite contains fibers which align at a constant angle to the field (T-type), giving rise to the "X" pattern of Figure 3e. It should be understood that the distributions of Figure 3 are obtained by illumination of a large area of the sample, and they are insensitive to sample translation. However, if the sample is rotated, the scattered light distribution also rotates. This is the basis of the measurement technique.

To obtain quantitative information from these scattered light patterns, a detector is used to measure the intensity of the scattered light at a fixed angle from the optical axis. The difference between the intensities at a maximum position and a minimum position is a measure of the amount of aligned fibers in the sample. A convenient method of examining the alignment behavior is to rotate the scattered light pattern so that its maxima and minima sweep over the detector area. This can be achieved by rotating the slide on which the orientations of aligned fibers have been permanently fixed. Another approach is to rotate a magnetic field slowly around a cell containing a free suspension of fibers in a liquid. The first technique is instrumentally simpler, and so this approach was investigated initially. The method was found to have some limitations, which prompted a fuller investigation of the rotating magnet system. For each system, the initial task was to determine the detection level for asbestos fibers.

SECTION 4

FIXED FIBER ALIGNMENT TECHNIQUE

4.1 EQUIPMENT DESIGN

The principle of the scattered light analysis technique is illustrated schematically in Figure 4. The sample is a transparent plastic film containing fibers which have been aligned magnetically. A beam of light from a laser is used to illuminate the aligned fiber sample, which is rotated about an axis coincident with the center of the beam. A photomultiplier detector is mounted so that its axis intersects the incident beam at the center of the sample. The angle of intersection, ϕ, can be varied. The detector output is a measure of the scattered light intensity for a particular value of the detector angle ϕ, and can be expressed as a function of θ, the angular rotation of the sample from the original magnetic field direction used during preparation.

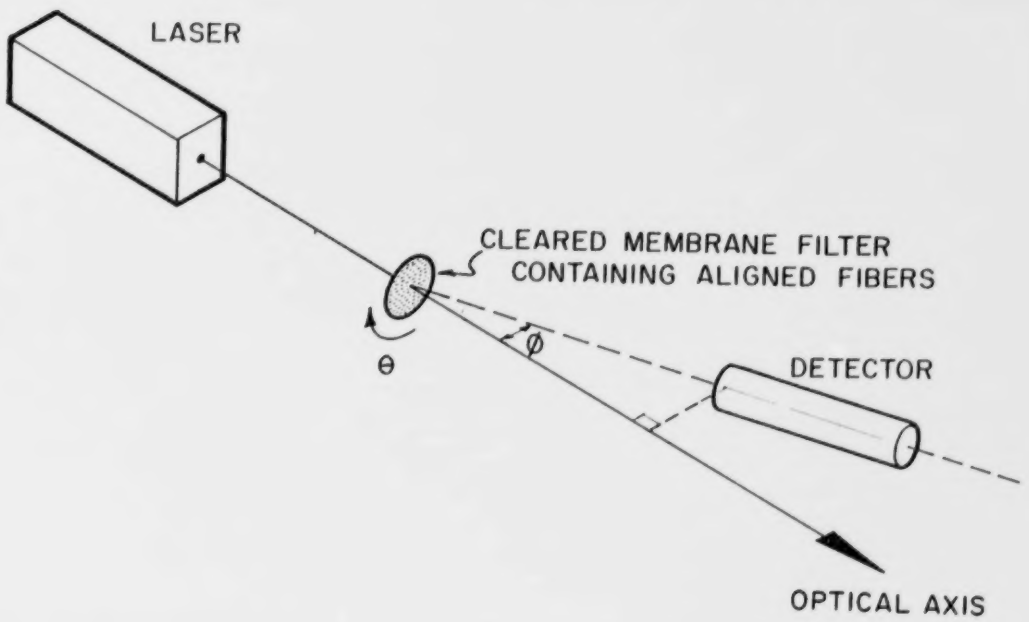

Figure 4. Schematic of system used for the analysis of light scattered from aligned asbestos fibers.

The actual instrumentation used is shown in Figure 5. The light beam of 514.5 nm wavelength from an argon ion laser was expanded to a diameter of approximately 1.5 cm. The diameter of the beam illuminating the sample could be varied using an iris. This arrangement allowed a large area of the sample to be illuminated with uniform intensity. The sample was mounted at the center of a turntable, as shown in Figure 6. The scattered light was detected by a photomultiplier assembly mounted on an arm which could be rotated about the center of the sample. The signal from the photomultiplier was fed to an oscilloscope for initial evaluation of the samples, and to an x-y recorder which gave permanent records of the scattered light distributions. The sample turntable could be rotated at different speeds to accommodate this dual display technique.

Figure 5. System for scattered light measurements of fixed alignment samples. The laser is on the lower level of the optical bench, and the beam is reflected by mirrors to the upper level. The beam is expanded before illuminating the sample, and forward scattered light is detected by the photomultiplier.

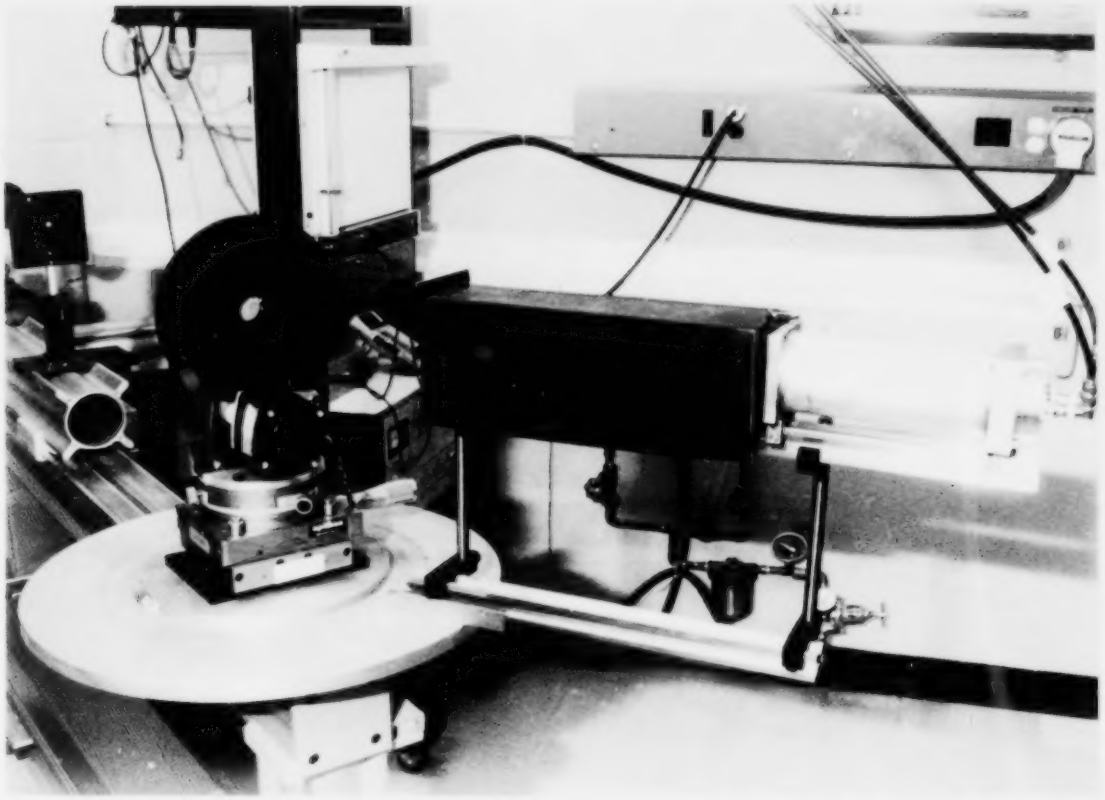

Figure 6. Sample turntable and photomultiplier.

4.2 SAMPLE PREPARATION

4.2.1 Filtration of Aqueous Fiber Dispersions

The sample preparation technique was designed to produce a membrane filter on which asbestos fibers were aligned by a magnetic field applied during a filtration procedure (referred to as magnetic filtration). In this technique a 25 mm diameter glass filtration assembly (Millipore Corporation, Cat. No. XX10 025 00) was located between the poles of an electromagnet, and a non-magnetic clamp was used to attach the filter reservoir. Suction for the filtration was provided by a water jet pump (aspirator). The filtration apparatus is shown in Figure 7. Fibers become aligned as the liquid passes through the magnetic field, and retain their orientation when collected on the filter surface. This technique has the advantage of allowing concentration of the fibers from a known volume of liquid onto the active area of the filter. The complete procedure is specified by steps (a) to (e).

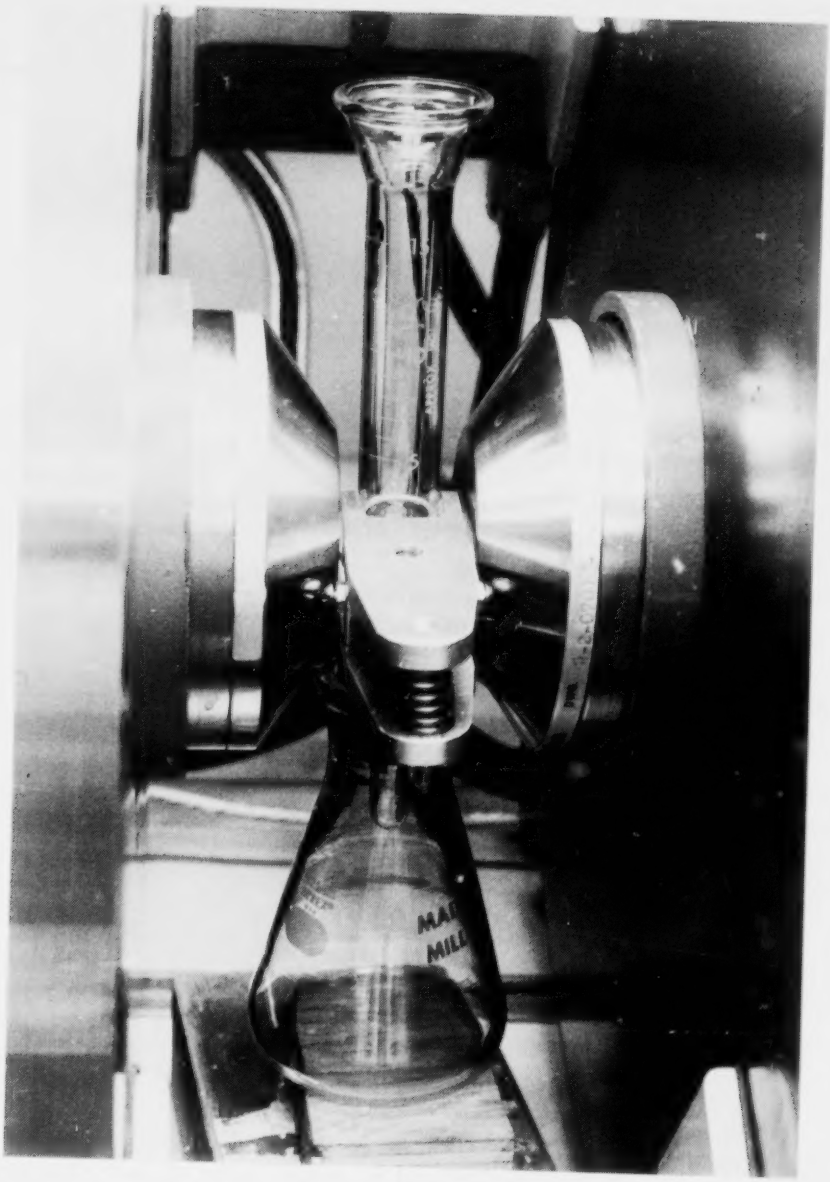

Figure 7. Filtration assembly located between the poles of an electromagnet.

(a) With a 0.22 μm pore size type GS Millipore^{R} filter mounted in the filtration assembly, the aspirator is turned on and the magnetic field is adjusted to the desired value (about 1.0 T).

(b) The desired volume of liquid is filtered through the assembly. The filtration rate should be restricted to ensure that the fibers have adequate time to become aligned before contacting the filter surface. The filtration rate can be adjusted by changing the applied vacuum. A filtration rate of about 10 mL/minute has been found to be satisfactory.

(c) The magnetic field is then turned off.

(d) A mark is made on the edge of the filter nearest to one pole of the magnet. This provides a record on the filter of the field direction during filtration.

(e) The filter is removed and dried for approximately 15 minutes at 70°C.

4.2.2 Clearing of Membrane Filters

The filter on which the aligned fibers have been deposited must be rendered transparent before it can be examined using the light scattering equipment. Since it was discovered that the detection level for the presence of fibers was dependent on the degree of filter transparency which could be obtained, several different preparation techniques were investigated. All of the filter clearing techniques involve collapse of the membrane filter sponge structure by exposure to acetone vapor. During this procedure the filter must not become distorted and the fibers must retain their orientations. To prepare a satisfactory sample the filter must be held in position on a flat substrate.

In the original technique, a clean glass microscope slide was used as a substrate for the filter. The slide was first dipped in a 20% solution of collodion in ethanol and allowed to stand for about 30 seconds, after which period the surface film became viscous. The filter was then placed onto this surface film, using a rolling action to inhibit formation of air bubbles between the glass slide and the filter. The filter was then collapsed by exposing its surface to acetone vapor. This was done by inverting the slide over a beaker containing acetone. When the filter had become transparent it was removed from the acetone vapor and allowed to stand for a few minutes, during which the filter plastic solidified.

For scattered light analysis, the filter was carefully removed from the glass slide after cutting one edge to release it. The clear plastic membrane obtained contained aligned fibers, and it

could be supported in a holder for scattered light analysis. Although the sample could be removed from the glass slide immediately after clearing, it generally peeled from the surface more easily if it was stored for about 24 hours after it had been removed from the acetone vapor.

Cleared filter samples prepared from unused filters were examined using the equipment described in 4.1. An index of the transparency of such a sample is given by measurement of the total forward scattered light intensity at a fixed angle from the optical axis. The limit of detection for asbestos fibers is in fact determined by the variation in the scattered light intensity from a blank sample as it is rotated. It is therefore desirable that this intensity and its variation with sample rotation be minimized, so that the scattered light intensity from filtered particulate material will form as large a proportion of the total signal as possible. Accordingly, measurements were made on a series of blank samples prepared by various techniques, and these were compared with values obtained from cleaned microscope slides, cover-slips and thin collodion membranes.

Initial measurements indicated that the collodion used to attach the membrane filter to the microscope slide was itself a source of scattered light, and alternative means of attachment were investigated. It was found that the buckling and distortion of a membrane filter during the acetone clearing procedure could be prevented if the pores of the filter were filled with a compatible, but acetone-miscible, solvent. The solvent used was 1,2-dichloroethane, and an optimum procedure was developed for clearing of 0.22 μm pore size type GS Millipore filters without disturbing the fiber alignment. In this procedure, a small amount of dichloroethane was first placed on a 5 cm x 7.5 cm microscope slide. The filter was placed on the dichloroethane and immediately transferred to a cleaned microscope slide. The edges of the filter were then rapidly attached to the slide using an acetone-based adhesive (nail polish). This step must be performed quickly, since the filter lifts from the slide as the dichloroethane evaporates. The method was rapid and effective in yielding filters which lay in contact with the slide surfaces. The filter was immediately cleared by exposure to acetone vapor.

In a study of acetone vapor clearing methods, it was found that the technique published by the Asbestos International Association[15] (AIA) yielded clearer filters than those produced by various modifications of the acetone vapor chamber method of Ortiz and Isom.[16] In the AIA method, the equipment shown in Figure 8 is used to direct a stream of acetone vapor onto the filter surface. Although the AIA clearing process was somewhat variable and the samples produced were found to yield a wide range of scattered light intensities, the actual values were lower than those given by any other technique tested.

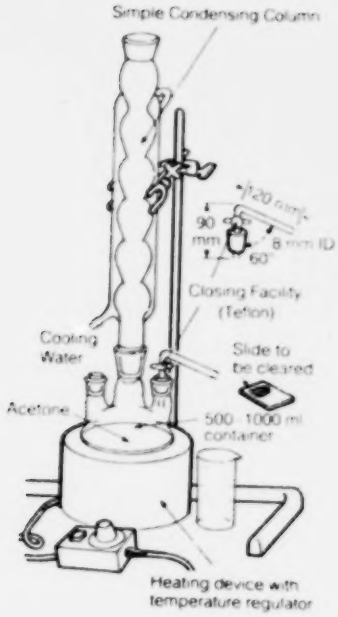

Figure 8. Equipment used to collapse membrane filters. (After AIA, 1979).

A summary of the measurements made is given in Table 1. It can be seen that scattered light from the glass microscope slide did not contribute significantly to the background intensity when compared with the values obtained for cleared membrane filters. Moreover, the collodion previously used to attach the filter to the glass slide scattered light strongly, and its use should therefore be avoided in the sample preparation.

The sample preparation procedure which produced the lowest background scattered light was to mount the filter by the dichloroethane technique and then to clear the filter using the AIA acetone vapor method. The variability of the scattered light signal obtained from a group of ten such preparations was measured; these results are shown in Table 2. The significant feature of the results is that, with one exception, all of the filters yielded two peaks in the scattered light profile of similar shape to those obtained for aligned fibers of chrysotile asbestos. When these peaks occurred in the same positions as those expected for chrysotile, they imposed a lower limit for the detection level. It was not possible to obtain a flat response from the majority of preparations.

TABLE 1. MEASUREMENT OF SCATTERED LIGHT FROM SAMPLE PREPARATION MEDIA

MEDIUM	BACKGROUND SIGNAL, mV	NOISE AMPLITUDE (peak-to-peak), mV
Cleaned Glass Microscope Slide	90 - 250	15 - 100
Cleaned Glass Cover-slip	300 - 900	75 - 150
50 nm Thick Collodion Membrane	400 - 1500	120 - 1000
0.22 µm pore size type GS Millipore Filter (AIA cleared)	3000 - 6000	150 - 1000
0.22 µm pore size type GS Millipore Filter (Vapor-chamber cleared)	9000 - 20000	500 - 1000
0.45 µm pore size PVC Copolymer Gelman Filter (cleared with a dioxane cyclohexanone solution)	8000 - 25000	1000 - 2000

TABLE 2. MEASUREMENT OF SCATTERED LIGHT FROM SAMPLES PREPARED BY THE DICHLOROETHANE-AIA TECHNIQUE

SAMPLE NUMBER	BACKGROUND SIGNAL, mV	NOISE AMPLITUDE (peak-to-peak), mV	NOISE PATTERN
1	1990	190	++
2	1760	120	++
3	1940	180	++
4	2170	300	++
5	3960	1000	+
6	2560	330	++
7	3280	750	++
8	2160	190	++
9	1720	310	++
10	1820	190	++

[+] An approximate sine curve with one peak per revolution.

[++] Scattered light peaks 180° apart which were very similar to and indistinguishable from those produced by chrysotile when the orientation is appropriate.

4.3 MEASUREMENTS AND RESULTS

The objectives of the measurements are as follows:

(a) to determine the sensitivity of the system using suspensions of the three asbestos varieties UICC crocidolite, UICC amosite and purified Union Carbide Calidria chrysotile, each dispersed in double-distilled water;

(b) to determine the effects of additions of non-fibrous particulate; and

(c) to investigate possible methods of improving the detection level, if required.

4.3.1 Measurement of Detection Levels for Asbestos Fibers Dispersed in Double-Distilled Water

Samples were prepared by filtration of a range of volumes of a stock dispersion of UICC crocidolite in double-distilled water. The procedure was repeated for both UICC amosite and Union Carbide chrysotile. Scattered light profiles were obtained for all of the samples. Figures 9, 10 and 11 show examples of the profiles obtained for filter loadings of about 15 ng/mm^2 of the three materials. It can be seen that for this filter loading there was a strong signal from the aligned fibers, which was easily detectable. When the filter loading was further reduced by a factor of 20 - 100, the profiles shown in Figures 12, 13 and 14 were obtained. The peaks were still easily detectable at these reduced concentrations, and would still be measurable if the fiber concentration were reduced by a further factor of 5. This indicates that in the absence of major proportions of other particulate material, a fiber concentration of about 0.1 ng/mm^2 would be detectable for any one of the three varieties.

The peak areas for all of the scattered light profiles obtained from each material were measured using a planimeter, and the areas expressed in arbitrary units were plotted as functions of mass concentrations and numerical fiber concentrations. The calibration curves obtained are shown in Figures 15 - 18.

In the results for crocidolite shown in Figure 15, it can be seen that for mass concentrations below 0.1 ng/mm^2 replicate measurements range over a factor of 8. At this concentration, the peaks from the fibers are sometimes difficult to separate from the noise and therefore this concentration can be taken as the approximate minimum detection level. Detailed detection level studies were not performed for amosite, but the patterns shown in Figures 16 and 17 are similar to that obtained from crocidolite. The data for chrysotile, shown in Figure 18, indicate that at low chrysotile concentrations, peaks are present which are unrelated

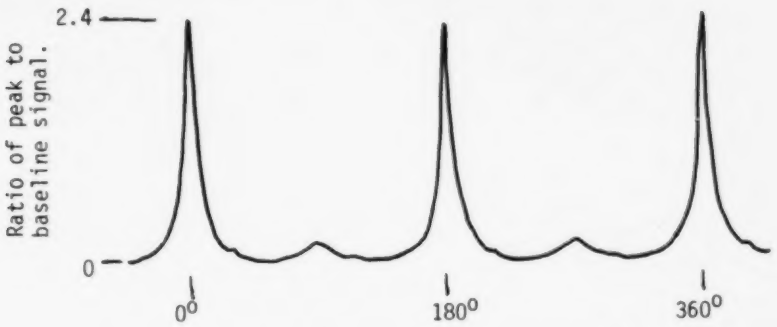

Figure 9. UICC Crocidolite: Scattered light profile obtained from a filter loading of 15 ng/mm^2.

Figure 10. UICC Amosite: Scattered light profile obtained from a filter loading of 16 ng/mm^2.

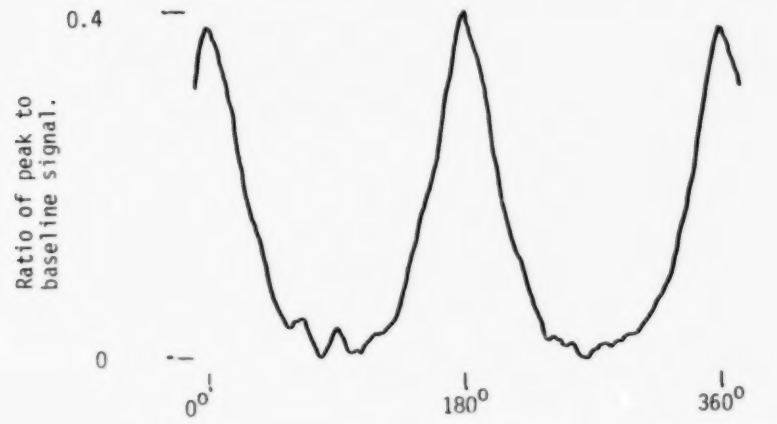

Figure 11. Union Carbide Chrysotile: Scattered light profile obtained from a filter loading of 12 ng/mm^2.

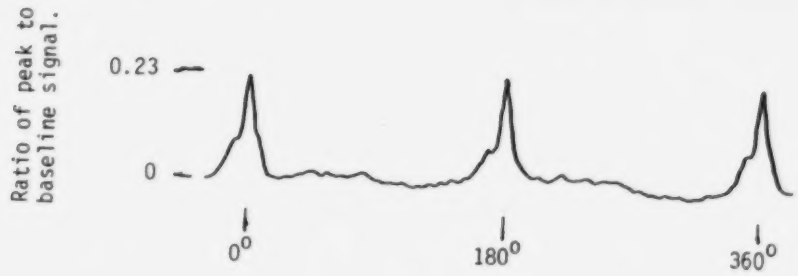

Figure 12. UICC Crocidolite: Scattered light profile obtained from a filter loading of 0.4 ng/mm^2. (Mass loading corresponds to 850 fibers/mm^2 of median length 0.6 μm).

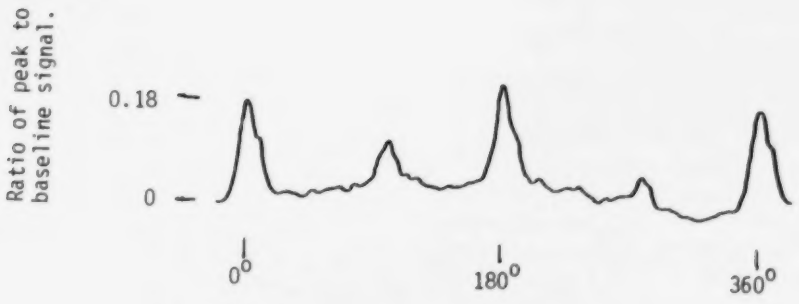

Figure 13. UICC Amosite: Scattered light profile obtained from a filter loading of 0.2 ng/mm^2. (Mass loading corresponds to 280 fibers/mm^2 of median length 1.0 μm).

Figure 14. Union Carbide Chrysotile: Scattered light profile obtained from a filter loading of 0.6 ng/mm^2. (Mass loading corresponds to 10^5 fibers/mm^2 of median length 1.0 μm).

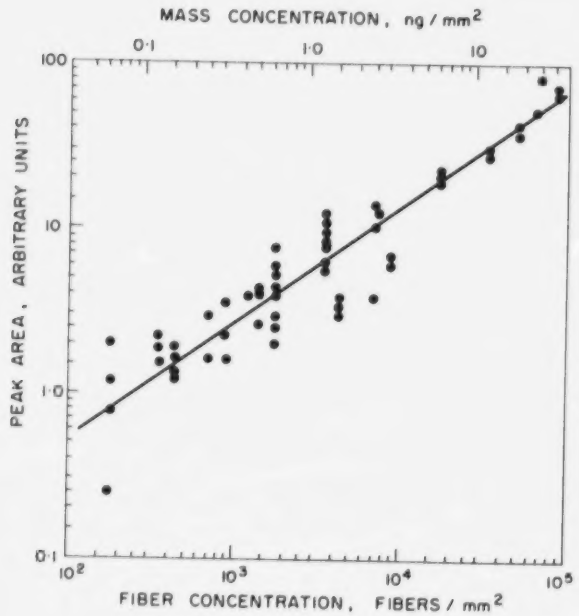

Figure 15. UICC Crocidolite: Area of P-fiber peak as a function of mass and fiber concentration on filter.

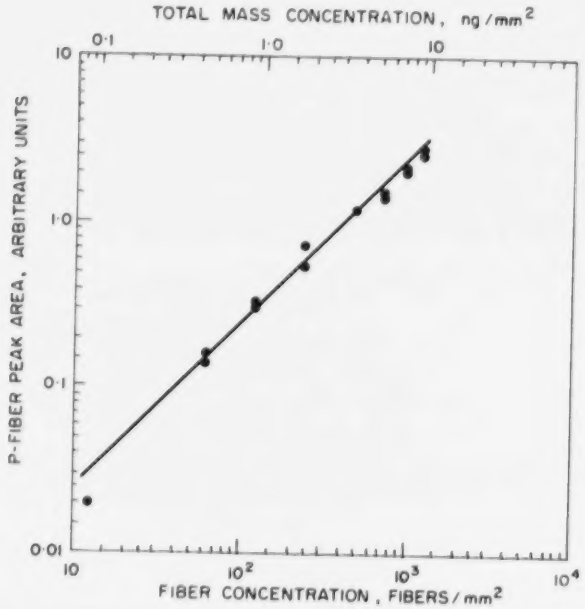

Figure 16. UICC Amosite: Area of P-fiber peak as a function of mass and fiber concentration on filter.

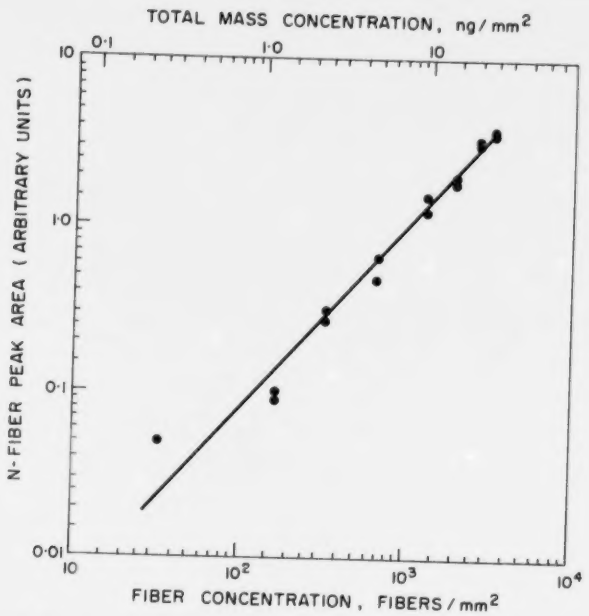

Figure 17. UICC Amosite: Area of N-fiber peak as a function of mass and fiber concentration on filter.

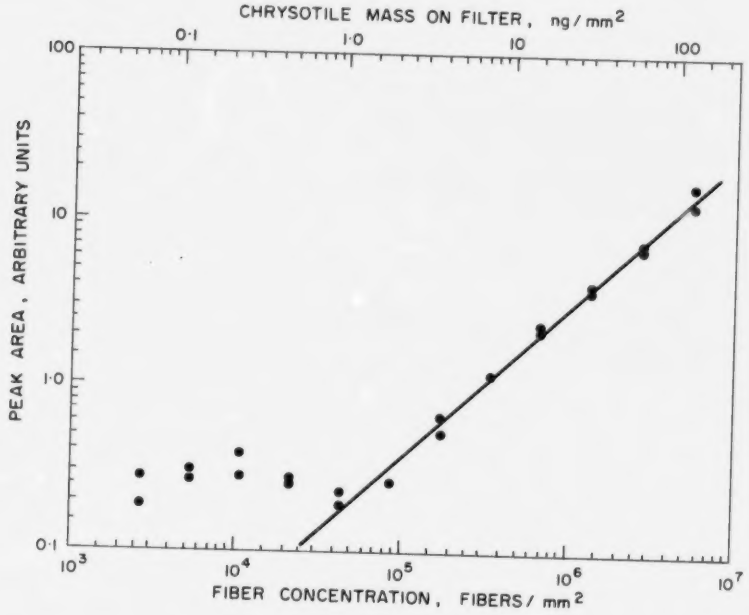

Figure 18. Union Carbide Chrysotile: Area of peak as a function of mass and fiber concentration on filter.

to the presence of chrysotile. Accordingly, peaks similar to those shown in Figure 14 should be interpreted with considerable caution.

For fiber concentrations greater than about 10^5 fibers/mm^2 or 1.0 ng/mm^2 there appears to be a direct relationship with peak area. At concentrations below these values, the peak areas maintained an approximate constant value similar to that observed at 10^5 fibers/mm^2, regardless of fiber concentration. It is thought that these are artifact peaks originating from residual structure in the collapsed filter, and that this residual structure defines a minimum detectable limit in these measurements. These results indicate that the method of filtering in a magnetic field, followed by collapsing of the Millipore filter, gives a detection limit for chrysotile of the order of 10^5 fibers/mm^2 or 1.0 ng/mm^2. Ten filter samples prepared with a 10^5 fibers/mm^2 loading of chrysotile further supported this value for the detection limit; only three yielded easily recognizable fiber peaks.

4.3.2 Effects of Non-Fibrous Particulate

To investigate the effects of non-fibrous particulate, various volumes of municipal drinking water containing 0.3 ng/mL of total insoluble solids were mixed with 5 mL aliquots of a 0.2 ng/mL dispersion of amosite, and the resulting dispersions were prepared for scattered light measurements. It was found that the effect of the non-fibrous particulate was to increase the value of the background intensity of the scattered light. The sizes of the peaks remained approximately constant. Figure 19 shows the scattered light profile for which the filter loading was approximately 50 ng/mm^2 of total insoluble solids and 1 ng/mm^2 of amosite. The experiments indicated that approximately 0.1% by weight of amosite as a proportion of total insoluble solids was still detectable.

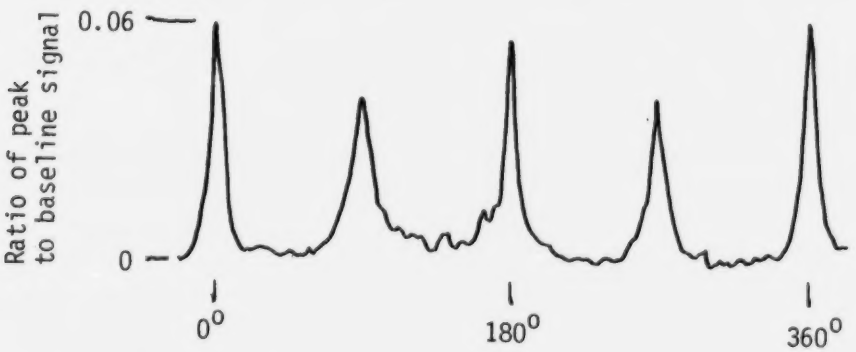

Figure 19. Scattered light profile showing peaks from amosite in municipal drinking water. Filter loading was 1 ng/mm^2 amosite and 50 ng/mm^2 total insoluble solids.

This conclusion is reasonable in view of the fact that most of the intensity of the scattered light originates from the filter itself. However, the results do indicate that at approximately the 0.2 ng/mm^2 level of an amphibole, the other components in this municipal water sample did not contribute any measurable interference to the determination of the fiber concentration.

4.4 MAGNETIC FIELD REQUIREMENTS FOR FIBER ALIGNMENT

Initial work has shown that crocidolite and amosite align very precisely in magnetic fields. It was found that even the residual magnetic field present when the magnet was not energized was adequate to produce some alignment effect on these fibers. In contrast, alignment of chrysotile filters requires much stronger fields. Because the higher value of the detection level which was obtained for chrysotile may have been a consequence of inadequate field strength, it was decided to investigate the minimum magnetic field requirement for efficient alignment of chrysotile fibers. Since the cost of the magnet escalates very rapidly with increase of field strength, it was also required to determine whether an increase of magnetic field strength above the minimum value required would yield a useful increase in the scattered light signal.

Aliquots of 10 mL volume from a 250 µg/L chrysotile dispersion were filtered at differing field strengths from 0.2 T up to 1.0 T in increments of 0.2 T. The resulting filter samples were prepared and the scattered light distributions measured. The areas of the scattered light peaks were measured and plotted against the magnetic field strength, giving the results shown in Figure 20. Maximum alignment was achieved for field strengths greater than 0.4 T. These results demonstrate good repeatability and show that 0.4 T is an adequate field strength for the magnetic filtration technique.

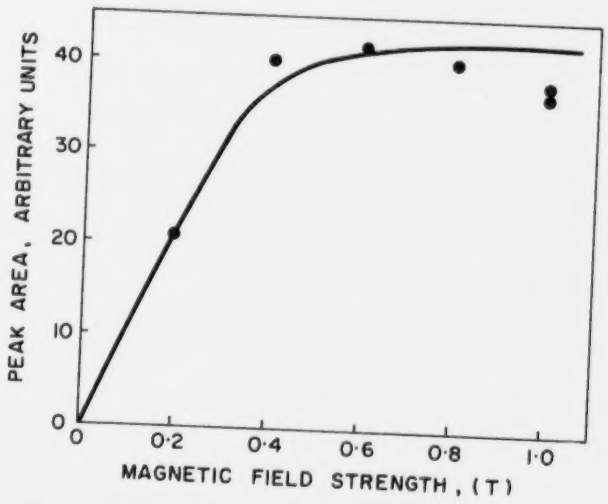

Figure 20. Union Carbide Chrysotile: Variation of peak area with magnetic field strength.

4.5 SIGNAL ENHANCEMENT TECHNIQUES FOR IMPROVEMENT OF DETECTION LEVELS

The measurements made using crocidolite and chrysotile fibers have indicated that the minimum concentrations which can be detected on filters were about 0.1 ng/mm^2 and 1.0 ng/mm^2 respectively. For detection of chrysotile at a level of about 1 ng/L in water, concentration of the chrysotile from 200 liters of water onto a filter of 200 mm^2 active area would be required. The presence of large proportions of other particulate in this volume of water would probably degrade the detection limit still further. A significant improvement in the detection level is therefore required.

Since it appears that the scattered light from a blank filter cannot be reduced below some minimum level, an alternative approach would be to enhance the scattered light signal from the aligned fibers.

4.5.1 Complete Dissolution of Filter Medium

The scattered light from the filter background could be eliminated if the fiber orientations could be retained while the filter itself was dissolved or oxidized. A number of different techniques were investigated, all of which were based on extraction replication of the filter surface. A thick layer of silicon monoxide was deposited by vacuum evaporation in order to fix the fiber orientations. The filter was then placed on a glass slide and procedures such as solvent extraction or low temperature ashing were used to remove the filter medium. All of these techniques failed to yield optically flat samples. Residual cracks and wrinkles in the thin film yielded large peaks in the scattered light unrelated to the presence of fibrous material. Accordingly, this approach was abandoned.

4.5.2 Electronic Noise Reduction

Electronic noise suppression techniques such as use of a lock-in amplifier were considered as a means of extraction of periodic information from the light scattering profiles. Unfortunately, their application to this problem is inappropriate, since the background signal variability from the sample is identical for each rotation. These techniques are only useful for extraction of periodic signals from a background of random noise, and in this case all of the variability in the sample has been permanently fixed in position so that it repeats itself periodically once per revolution.

4.5.3 Use of Reflective Scattering Techniques

One way to avoid the limitation of detection level imposed by the residual internal structure of the cleared membrane filter would be to arrange the equipment so that reflective scattering from the filter surface is measured. In the early work on the magnetic alignment technique a Nuclepore capillary pore filter was used to

filter the fiber dispersion, after which a coating of gold was applied to the filter surface either by vacuum evaporation or by sputtering. The reflected scattered light intensity at an angle of about 30° from the optical axis was measured. Although strong signals from aligned fibers were obtained, reflective scattering was found to be very sensitive to imperfections on the filter surface. In particular, scratches on the filter surface were found to yield very large spurious peaks in the scattered light profiles.

The surface imperfection problem was reduced by using a Millipore filter and collapsing the structure in the same way as for the forward scattering technique. However, spurious peaks from many of the samples were still observed and at that time the technique was abandoned. At the improved detection levels already achieved by the forward scattering technique, the spurious peaks associated with reflective scattering would present an even more serious obstacle to reliable measurements.

4.5.4 Radiofrequency Plasma Etching of Filters

During collapse of the membrane filters by exposure to acetone vapor, many of the fibers are known to become totally embedded in the filter plastic. This reduces their contribution to the scattered light signal. Fibers embedded in the filter can be brought to the surface by etching the sample in an R.F. plasma asher. In order to evaluate the potential of this procedure for signal enhancement, a set of filter samples was prepared which had a 3500 fibers/mm^2 loading of aligned crocidolite fibers. The scattered light profile of each sample was measured. The samples were then exposed to different etching times ranging from one to eight minutes at an R.F. power level of 50 watts, after which the scattered light profile of each was recorded again. The results are summarized in Table 3. For a two-minute etching time the peak height was found to increase by a factor of 2.2, which was the maximum improvement obtained. Further increase of etching time up to about 6 minutes resulted in a gradual reduction of peak height, after which point there was a sudden drop to about 0.14 of the initial aligned fiber peak. The background scattered light intensity was also found to increase with etching time. These results suggest that:

(a) the optimum etching time was about 2 minutes;

(b) the increase in background intensity was due to development of structure on the filter surface;

(c) the sudden loss of peak height may be due to detachment, loss or disturbance of fibers when the sample was excessively etched.

A similar experiment was performed with filters which had loadings of 10^5 fibers/mm^2 of aligned chrysotile fibers. For an etching

TABLE 3. THE EFFECT OF R.F. PLASMA ETCHING ON ALIGNED CROCIDOLITE FIBER SAMPLES

SAMPLE NUMBER	BEFORE ETCHING		ETCHING TIME	AFTER ETCHING		PEAK HEIGHTS RATIO After/Before
	Background Signal, Volts	P-Fiber Peak Height, Volts		Background Signal, Volts	P-Fiber Peak Height, Volts	
1	3.9	1.33	1 min.	4.3	2.05	1.54
2	4.4	2.89	2 min.	8.8	6.40	2.21
3	4.4	3.68	3 min.	12.5	6.80	1.85
4	5.1	5.36	4 min.	16.1	8.90	1.66
5	5.1	5.37	5 min.	22.4	7.25	1.35
6	4.4	4.76	6 min.	31.3	0.66	0.14
7	4.4	5.14	7 min.	32.3	0.22	0.04
8	5.0	4.53	8 min.	32.4	0.15	0.03
9	4.6	4.39	-	-	-	-

time of 1½ minutes the peak height was found to increase by a factor of 3.5, while the background intensity increased by a factor of 2. For longer etching times the peaks at 0° and 180° became unequal in height.

It is clear that although some improvement in the scattered light signal can be obtained using the plasma etching technique, it does not offer significant potential for the major improvement of detection level which is required.

4.5.5 Shadowing of Particulate by Vacuum Deposition of Opaque Films

Angular asymmetry of the scattered light intensity from the cleared membrane filter is responsible for evaluation of the minimum detection limit. The effect of this can be eliminated by application of an opaque layer on the filter except in those areas occupied by particles. Such a layer would eliminate the contribution of the substrate to the scattered light signal. An opaque layer of either gold or aluminum can be applied by vacuum deposition, either normal to the filter surface or at some other angle. If the deposition is applied at normal incidence to the filter surface, the layer will be continuous except at the edges of the particles; if it is applied at some other angle, uncoated areas will occur on the filter surface where it is shielded from the evaporation source by the particles. It was thought that large improvements in the detection limit might be achieved by correlating the direction of deposition of the opaque film with the alignment direction expected for the fibers.

Experiments were conducted with opaque evaporated gold coatings. Some filter samples were coated at normal incidence, and others were coated at 45° incidence. The gold evaporation source was arranged so that the P-fibers were oriented with their lengths perpendicular to the evaporation direction. This geometry caused the P-fibers to produce uncoated slits on the filter surface, the dimensions of which were roughly the same as those of the fibers, while the rest of the filter was rendered opaque.

The results obtained from experiments conducted using aligned fiber samples of crocidolite and chrysotile are shown in Table 4. Significant improvements in peak to background ratios were obtained, but it was found that signals from non-fibrous particulate were generated which were similar to those from fibrous material. It is possible that further investigation of the technique, using two evaporation directions and signal processing, could eliminate the signals from the non-fibrous components. However, the technique was abandoned in favor of the liquid suspension technique described in Section 5.

TABLE 4. IMPROVEMENTS IN PEAK/BACKGROUND RATIO PRODUCED BY GOLD COATING

SAMPLE TREATMENT	PEAK/BACKGROUND RATIO		IMPROVEMENT RATIO
	Before Treatment	After Treatment	
Crocidolite, Gold Coated at Normal Incidence	0.32	2.14	6.7
Crocidolite, Gold Coated at 45° Incidence	0.54	4.00	7.4
Chrysotile, Gold Coated at Normal Incidence	0.22	1.76	8.0

4.6 EVALUATION OF THE FIXED FIBER ALIGNMENT TECHNIQUE

The best sensitivity achieved using this technique was about 0.08 ng/mm^2 of crocidolite and 1 ng/mm^2 of chrysotile. If a filter of 200 mm^2 active area is used, the minimum filter loadings detectable are 16 ng and 200 ng respectively. For chrysotile at an initial concentration of 1 ng/L,

concentration of the fibers from 200 liters of water would be needed to achieve the minimum detection limit. Even assuming a further order of magnitude improvement by the gold coating technique to be possible, the target detection level of 0.2 MFL or 1 ng/L could not be achieved. In a typical waterborne fiber size distribution, a crocidolite fiber concentration of 0.2 MFL corresponds approximately to 70 ng/L. To obtain a filter loading of 16 ng would require filtration of about 230 mL of water, which is marginally possible for relatively clean water. However, the target mass concentration of 1 ng/L is still not possible, since it would require filtration of 16 liters of water to achieve this detection limit.

SECTION 5

DYNAMIC FIBER TECHNIQUE

In this experimental arrangement the asbestos fibers are suspended in a liquid during the measurement. A magnetic field rotates around the liquid suspension, and the fibers also rotate, maintaining their orientation with the field direction. The forward scattered light intensity is measured at a fixed angle to the optical axis. In this system the problems associated with variability of the light scattered by the rotating filter, in the fixed fiber measurement system, are eliminated since only the fibers themselves rotate. Furthermore, the scattering is random for individual particles which are not affected by the magnetic field but move under Brownian motion only.

5.1 EQUIPMENT DESIGN

A schematic diagram of the equipment is shown in Figure 21. The fiber suspension is contained in a cylindrical quartz spectrophotometer cell of 5 mL volume and 2 cm path length. The magnet has a field strength of 0.9 T across a gap of 2.5 cm; since no suitable permanent magnets are commercially available it was necessary to construct this. The magnet rotation system was also constructed, and operates at speeds of 60 rpm down to 1.0 rpm. In this system, the signal from the photomultiplier detector is fed to a small computer and the scattered light profile is displayed on the computer video screen. This use of a computer allows much more flexibility when measuring the scattered light and analyzing the patterns produced. In particular, scattered light intensity data can be accumulated over a number of revolutions of the magnet, thus permitting averaging of the effects of random scattering from particulate other than fibers. This "dynamic fiber" scattered light measurement system is shown in Figure 22. Figure 23 shows the detail of the rotating magnet and detection optics. The instantaneous position of the magnet is detected by two optical encoders shown in Figure 24, one to count revolutions and another to count the 212 divisions within a single revolution. The sample loading mechanism consists of the cannon-shaped device shown in Figure 25, which accommodates the sample cell on the end. The cannon device is moved horizontally so that the sample is between the poles of the magnet. The light beam passes down the axis of the hollow cannon tube.

The operating procedure for the equipment is very simple. The liquid sample is first loaded in the system and positioned between the poles of the magnet. The magnet rotation is initiated, and the computer derives the angular velocity by timing one revolution. The intensity of the scattered light is measured at each of the 212 positions

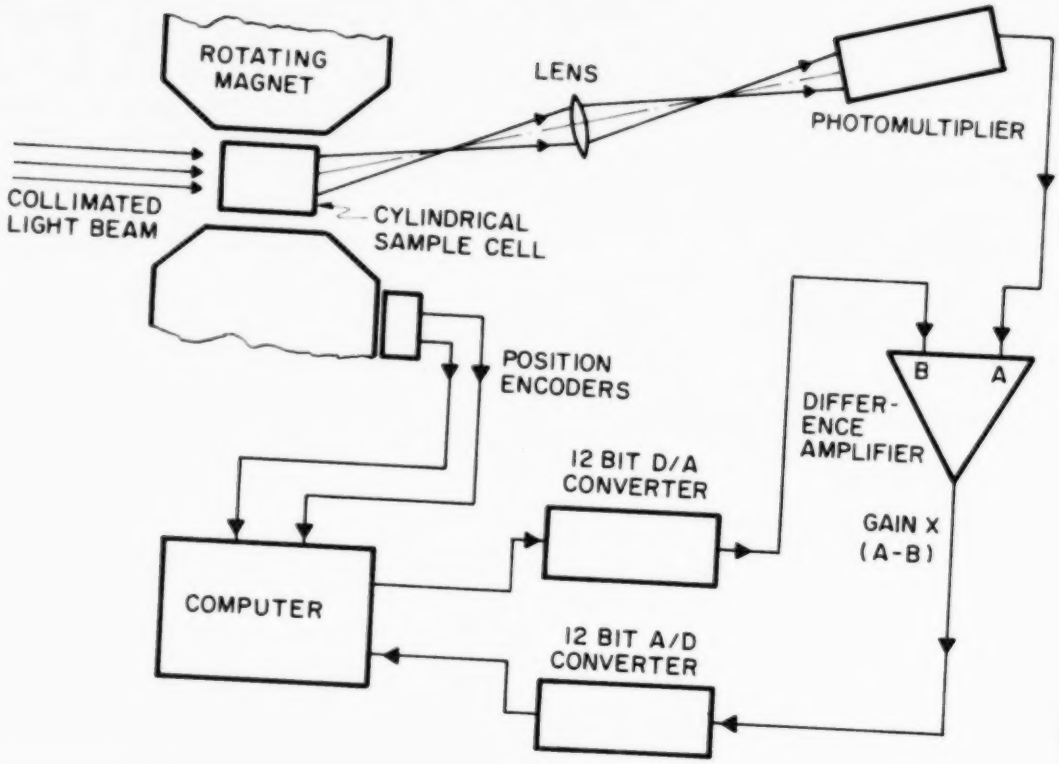

Figure 21. Schematic of equipment used for analysis of light scattered from magnetically-aligned fibers in liquid suspension.

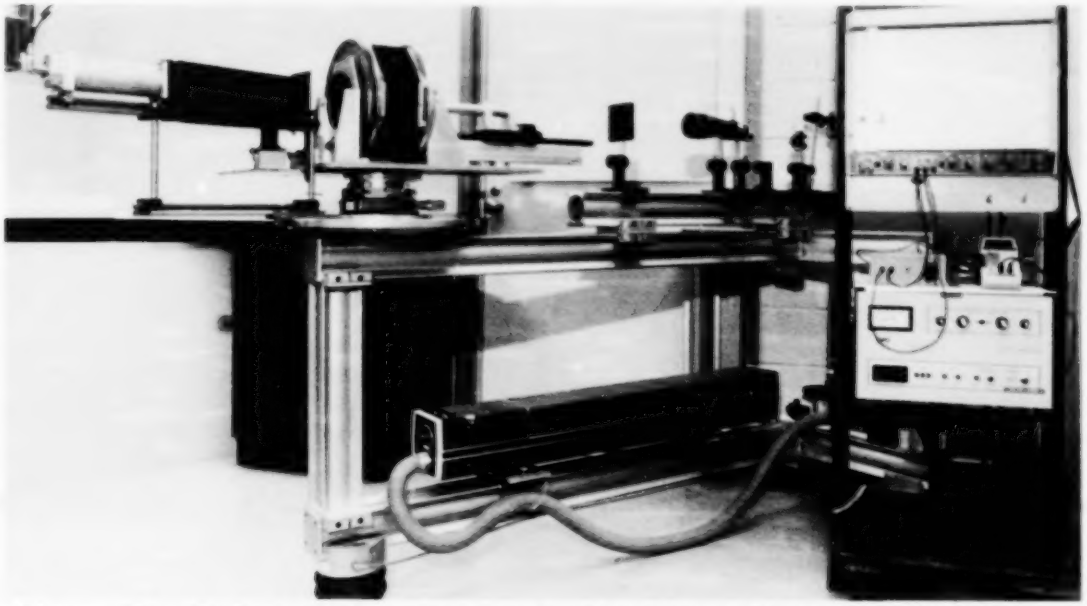

Figure 22. Equipment for measurement of scattered light intensities from fibers rotating in liquid suspensions.

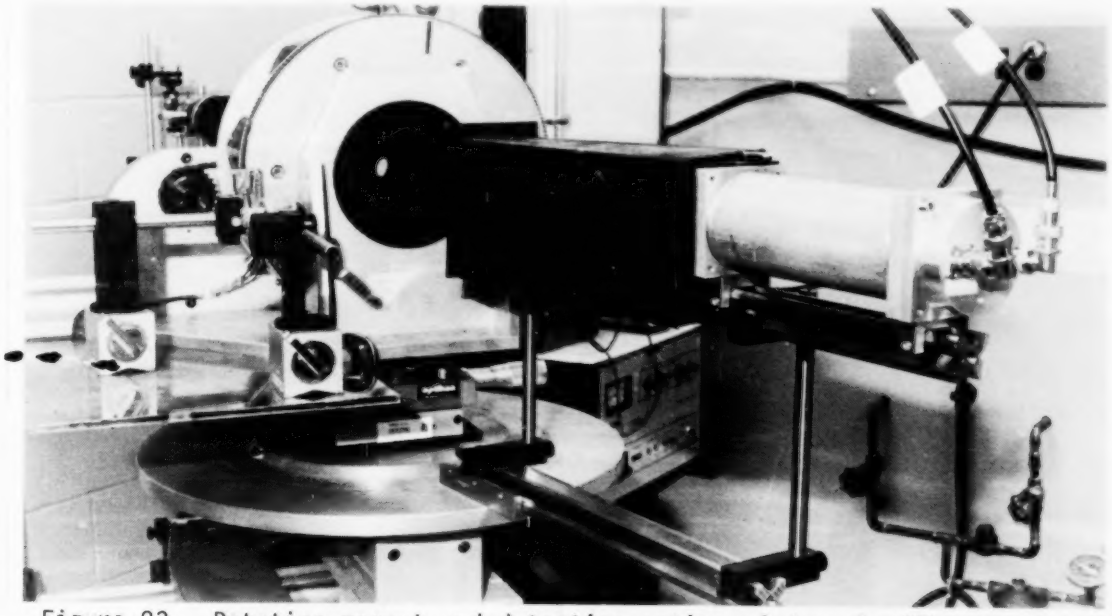

Figure 23. Rotating magnet and detection optics of dynamic fiber system. The lens is located at an angle of 12° from the optical axis and detects scattered light within 10^{-2} steradians. The lens is arranged so that the sample is imaged in the plane of the photomultiplier cathode.

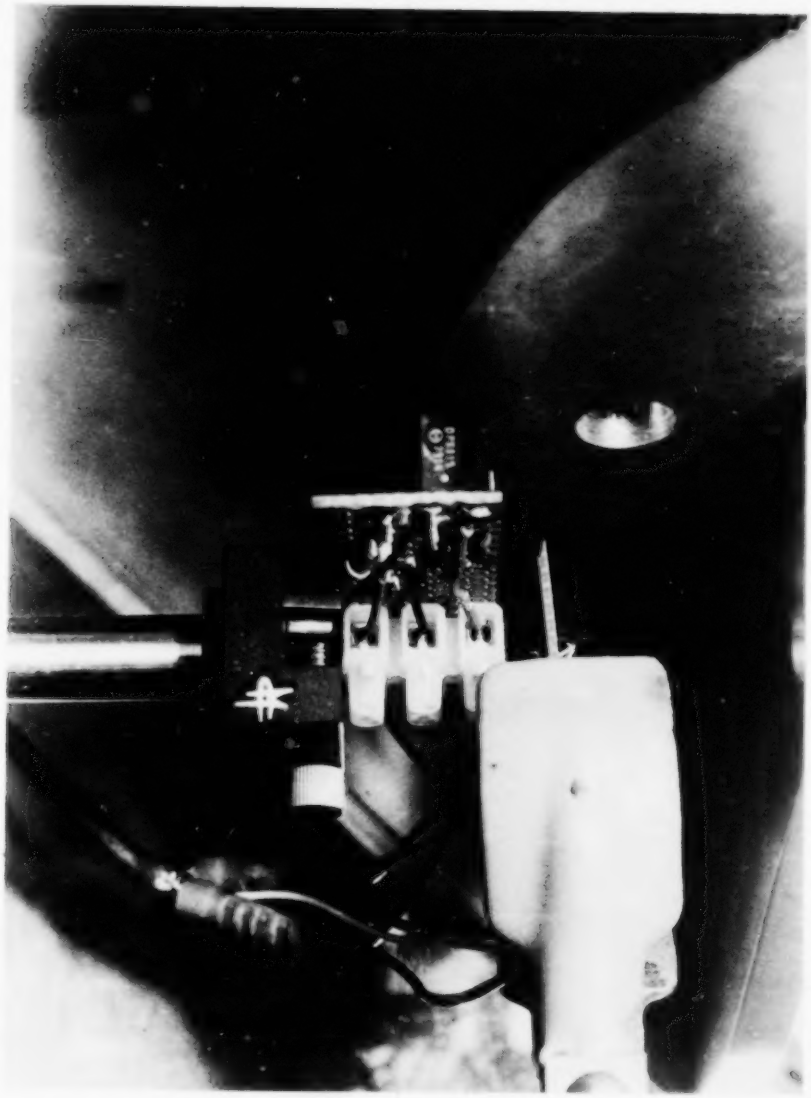

Figure 24. Position encoder located on magnet periphery used to communicate magnet position to the computer.

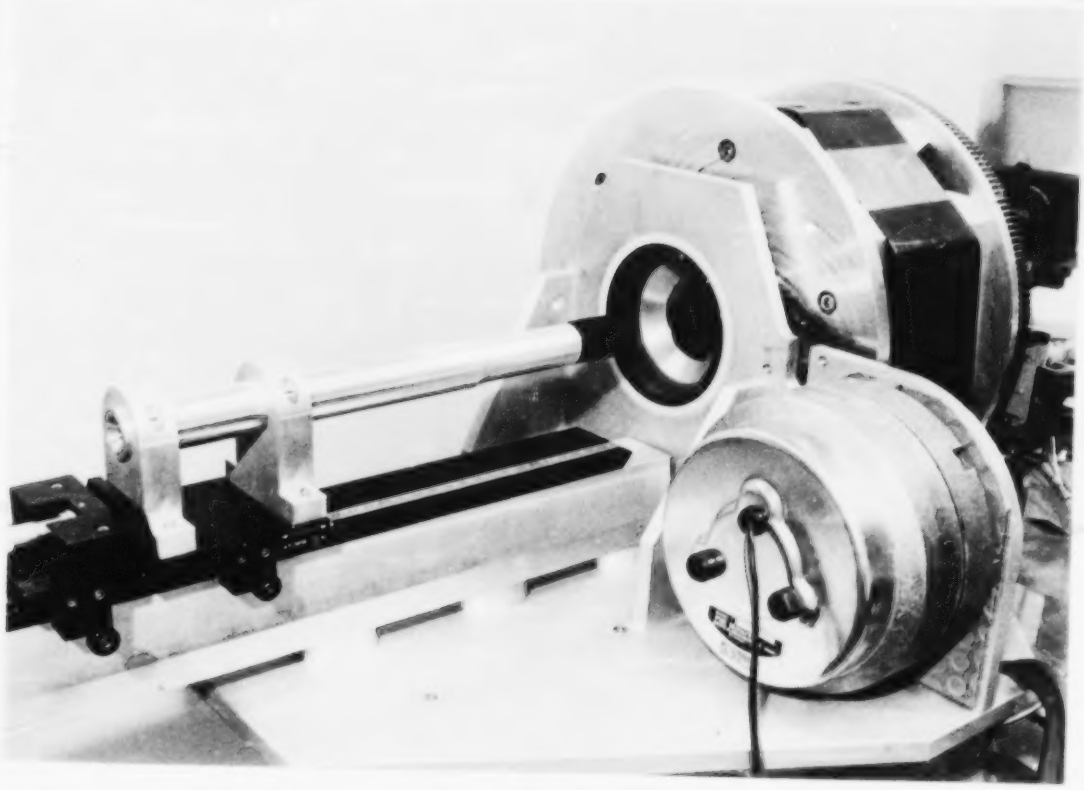

Figure 25. Sample loading mechanism.

within one revolution. The average value is transmitted to a difference amplifier, the gain of which is then adjusted so that peaks are amplified to about 1 - 5 volts. The output of the difference amplifier at each of the 212 positions for a single rotation is then recorded. Data from a specified number of revolutions of the magnet are accumulated and averaged. The scattered light profile can then be displayed on a video terminal or plotted.

5.2 SAMPLE PREPARATION

The fiber dispersion in water is placed in the spectrophotometer cell and measured directly. Where fiber concentrations are low, either non-selective or selective pre-concentration may be necessary. These techniques are considered in Section 6.

5.3 MEASUREMENTS AND RESULTS

It was found that there are three types of particulate which are relevant to the measurement technique:

(a) fibers which align with and rotate with the magnetic field;

(b) particles of equant or random shapes which rotate with the magnetic field; and

(c) fibers or particles of equant or random shapes which do not respond to the magnetic field.

The fibers in category (a) produce scattered light profiles which have peaks. At high magnet rotation speeds fibers may lag behind the orientation they would assume in a stationary field. Category (b) particles always produce broad scattered light peaks corresponding to alignment at 45°. Surprisingly, glass particles fall into this category. Category (c) particles simply contribute to a uniform background scattered light signal. Some particles of (b) and (c) are usually present in all samples, and certainly they will be present in environmental water samples.

The scattered light profiles obtained for three varieties of asbestos were examined to confirm that the dynamic fiber technique would produce data comparable with that from the filtration method. Figures 26, 27 and 28 show the profiles for UICC crocidolite, UICC amosite and Union Carbide chrysotile respectively. Although the curves for the two amphibole varieties were similar to those obtained from the filtration method, the chrysotile peaks were observed to lag behind the magnetic field by about 10° under the conditions of this measurement.

5.3.1 Measurement of Blank Samples

One of the most challenging problems in the use of this equipment was to obtain a satisfactory blank profile. The system is extremely sensitive to suspended particulate in the sample, and it was found that two effects initially prevented achievement of a flat profile which did not contain scattered light peaks.

The first effect was the presence of a sinusoidal signal displaying one cycle per revolution of the magnet. To investigate this effect, a source of scattered light which did not vary with magnet rotation was required. This was conveniently arranged by positioning a thin sheet of polyethylene in place of the spectrophotometer cell. It was found that variation in stray magnetic field during rotation of the magnet was altering the gain of the photomultiplier. The effect could not be eliminated without a significant revision of the experimental equipment, but it was minimized by a combination of magnetic shielding and re-positioning of the photomultiplier. At high values of amplifier gain it was found that the baseline of the signal still displayed a slight sinusoidal variation, which could then be removed by profile subtraction to leave only the relevant signal.

The second effect was a consequence of the inability to produce absolutely particle-free water. The only water suitable for preparation of low background samples was found to be water double-

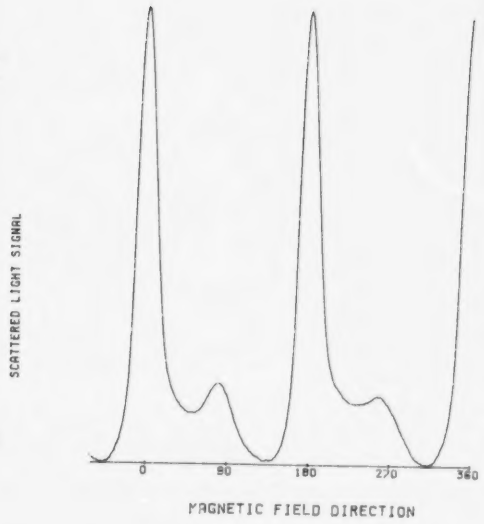

Figure 26. UICC Crocidolite: Dynamic scattered light profile.

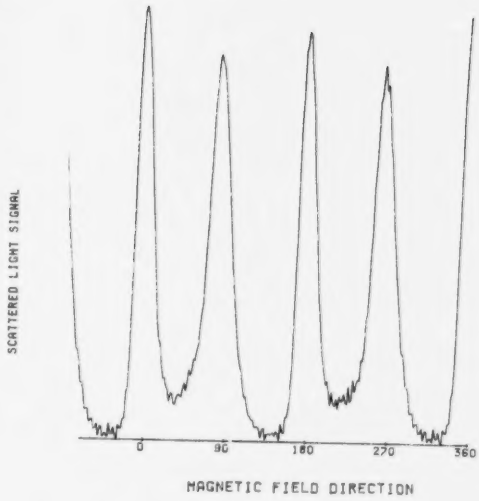

Figure 27. UICC Amosite. Dynamic scattered light profile.

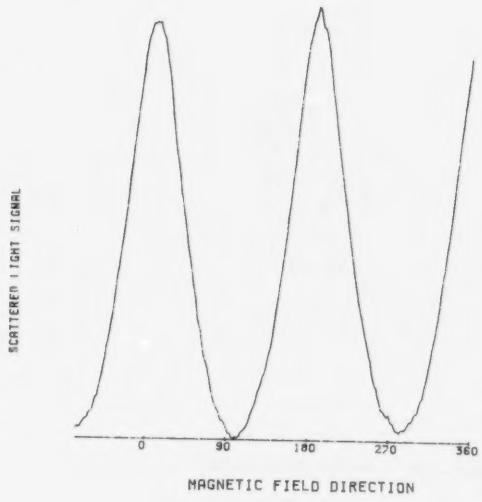

Figure 28. Union Carbide Chrysotile: Dynamic scattered light profile.

distilled in glass, with precautions being taken not to disturb ground glass joints during the distillation. Filtered water was in no way satisfactory, since in the context of these measurements filtration merely replaces one kind of particulate with another which originates from the downstream surfaces of both the filter and the filtration equipment. For the low background work, double-distilled water from a Corning MEGA-PURE™ still has been found satisfactory, however, it must be collected directly in borosilicate glass bottles having plastic screw caps with Teflon® liners.

To obtain a blank scattered light profile, the "particle-free" double-distilled water must be handled only in a laminar flow hood. As many as ten successive washings of the cell may be necessary before a sufficiently low level of particulate contamination is achieved. Ultrasonic treatment should be avoided, since this tends to generate particulate.

5.3.2 Measurement of Detection Levels for Asbestos Fibers Dispersed in Double-Distilled Water

Using dispersions of UICC crocidolite and Union Carbide chrysotile, the system was calibrated to obtain values for the minimum detection limits. The calibrations were performed by preparing a series of fiber dispersions from serum bottles of standard fiber suspensions. The serum bottles had concentrations of 140 MFL for crocidolite and 200 MFL for chrysotile, and the test dispersions were prepared by dilution of these with "particle-free" water. The concentrations were spaced logarithmically at intervals of a factor of 3 from the serum bottle concentration down to about 0.2 MFL. The spectrophotometer cell was loaded with each dispersion in turn, starting with the lowest concentration and working upwards to avoid cross-contamination. The scattered light profile of each dispersion was measured for 10 to 20 revolutions at a magnet speed of 10 rpm for crocidolite, and for 5 revolutions at 1 rpm for chrysotile. Figures 29 and 30 illustrate the variation in scattered light signal with fiber concentration.

Because of the effect of the magnetic field on the photomultiplier, and the response of the non-fibrous contamination to the rotating field, it is necessary to employ profile subtraction techniques to extract the relevant peaks for very low fiber concentrations. For these calibration experiments the subtraction was performed manually; a computer program has since been written to do subtractions. The calibrations obtained are shown in Figures 31 and 32, in which peak areas are shown as functions of both numerical and mass concentrations. The detection level for crocidolite was found to be about 0.5 MFL, and for chrysotile about 5 MFL. These detection levels apply to the fiber dispersion in the spectrophotometer cell, and correspond to mass concentration detection levels of about 180 ng/L and 30 ng/L for crocidolite and chrysotile respectively.

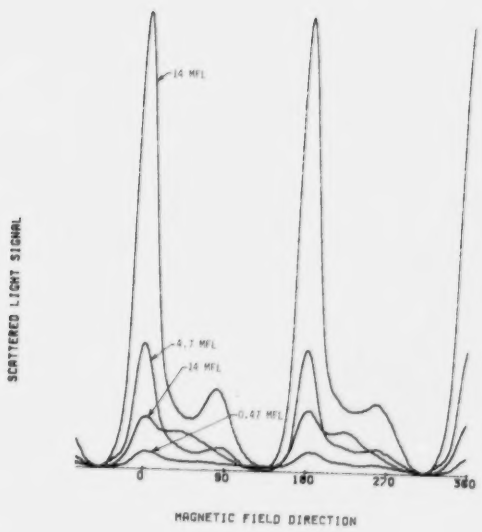

Figure 29. UICC Crocidolite: Variation of scattered light profile with fiber concentration.

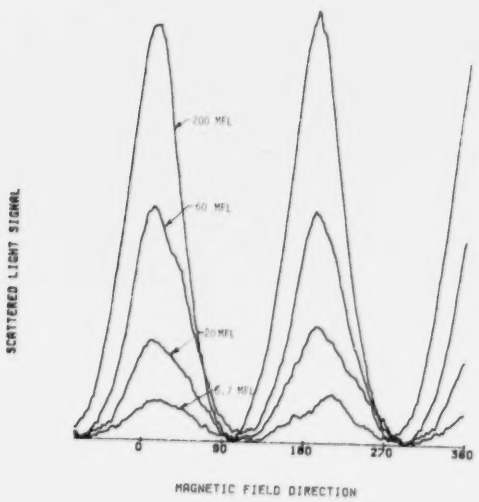

Figure 30. Union Carbide Chrysotile: Variation of scattered light profile with fiber concentration.

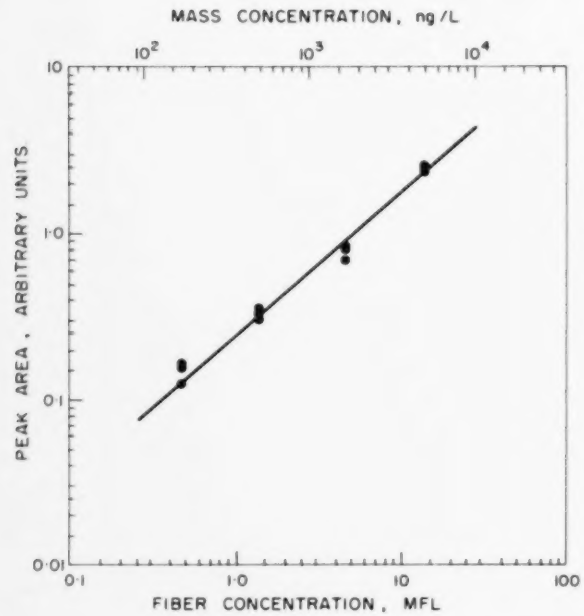

Figure 31. UICC Crocidolite: Area of P-fiber peak as a function of mass and fiber concentration.

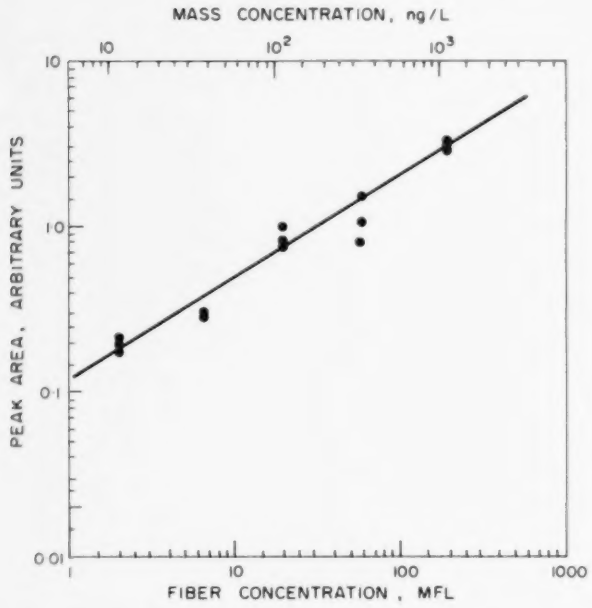

Figure 32. Union Carbide Chrysotile: Area of peak as a function of mass and fiber concentration.

In general, to achieve the target detection level of 0.2 MFL or 1 ng/L, some selective or non-selective fiber concentration will be necessary. Although the dynamic fiber analysis technique is significantly more sensitive than the filtration method, the ability to detect asbestos fibers can be degraded by the presence of some other types of particulate.

5.3.3 Effects of Non-Fibrous Particulate

Figure 33 shows the profile obtained from borosilicate glass particulate in water. This material rotates with the magnetic field and gives rise to broad peaks at 45° and 225°. This effect was not noticed when using the fixed fiber alignment technique, probably because it was below the detection level of the method and perhaps also because any preferred orientations of particles having random shapes would be disturbed when they contacted the filter.

The origin of the peaks has not been fully investigated, but can be explained if the particles adopt orientations such that their longest dimensions are parallel or normal to the magnetic field direction. The facets of the particles would scatter light preferentially throughout a broad angle, centered on ± 45° to the magnetic field direction. This would still occur if the particles had complete rotational freedom about their axes parallel to the magnetic field.

Non-fibrous particulate which does not respond to the magnetic field contributes only to the constant component of the scattered light intensity.

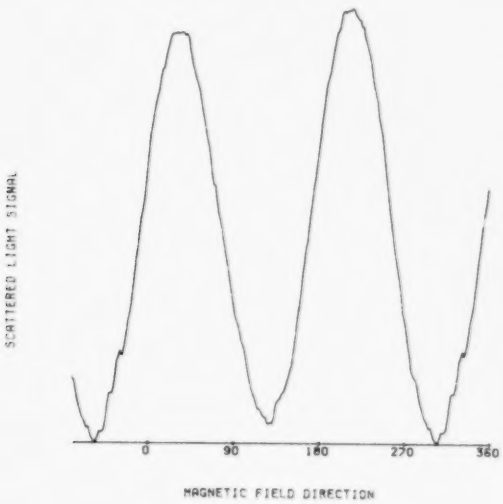

Figure 33. Scattered light profile of borosilicate glass particle suspension.

5.4 EVALUATION OF THE DYNAMIC FIBER TECHNIQUE

Of the various approaches examined, the rotating magnet system is capable of achieving the lowest detection limits and has the most potential for future development. At the lowest fiber concentrations of interest, other particle species present in even very clean water contribute significantly to signals which overlap the peaks from some types of asbestos fiber. General particulate which rotates with the magnetic field yields peaks corresponding to an alignment direction of 45° to the field. However, profile subtraction techniques can be used to extract the peaks originating from asbestos fibers, which always occur either at 0° and 180°, or at 90° and 270°. The system is capable of detecting a mass of 1 ng for crocidolite or 0.2 ng for chrysotile in a volume of 5 mL. With some pre-concentration of the water sample, it will be possible to detect 0.2 MFL or 1 ng/L of either material. Pre-concentration techniques are discussed in Section 7.

SECTION 6

ALIGNMENT MODES OF SELECTED MINERAL SPECIES IN MAGNETIC FIELDS

The alignment modes of UICC crocidolite, UICC amosite and UICC chrysotile have already been described in Section 3.1. The studies reported in Sections 4 and 5 have been conducted using UICC crocidolite, UICC amosite, and refined Union Carbide Calidria chrysotile. For calibration purposes, it was considered that the purified chrysotile would be more suitable than the UICC chrysotile.

The alignment modes of a selected group of minerals were determined in order that:

(a) potential interferences with the measurement of an asbestos fiber dispersion can be specified; and,

(b) the different alignment modes can be used as means of identification where possible.

Aqueous dispersions of a range of fibrous minerals were prepared for determination of their alignment modes using the dynamic fiber method. Other fibrous and non-fibrous minerals related to the primary varieties were also examined in the same way. The scattered light profiles are shown in Figures 34 - 81.

It is important to recognize that these profiles are qualitative, and indicate only the possibility of interference. Some of the materials, such as halloysite, did not appear to display strong alignment and on an equivalent mass basis may not constitute an interference with the measurement of other fibrous material. Some of the scattered light profiles contain contributions from other particulate which has rotated with the magnetic field, similar to the effect displayed by borosilicate glass particles. These contributions could be removed by a profile subtraction technique.

The following general conclusions can be drawn from the scattered light profiles of the selected minerals.

(a) All varieties of chrysotile behave in the same way; they display broad P-peaks which lag behind the magnetic field.

(b) Antigorite can be discriminated from chrysotile; the antigorite displays relatively sharp N-peaks.

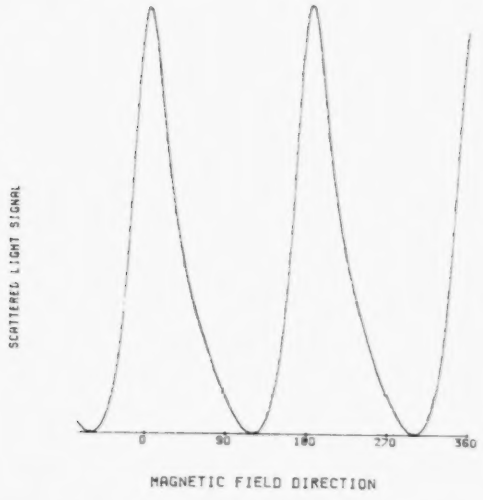

Figure 34. Chrysotile (UICC Canadian)

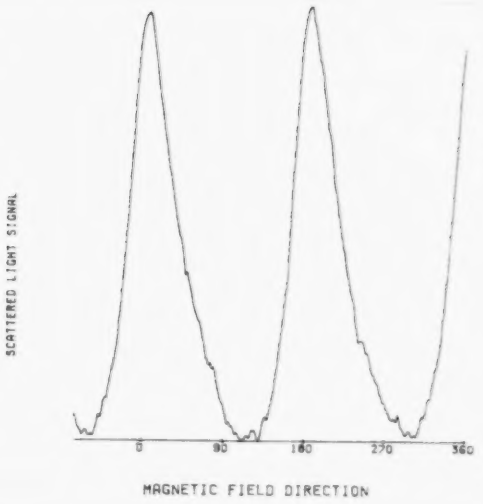

Figure 35. Chrysotile (UICC Rhodesian)

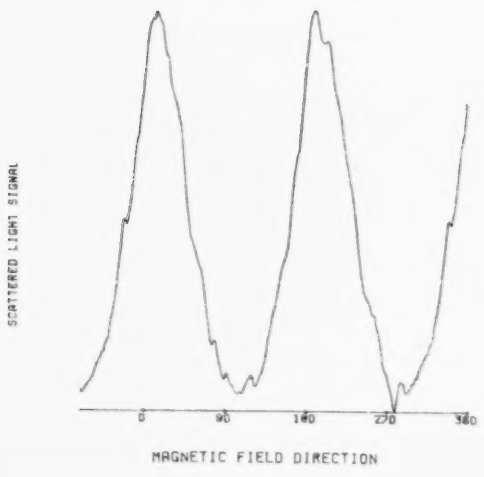

Figure 36. Chrysotile (Thetford, Quebec)

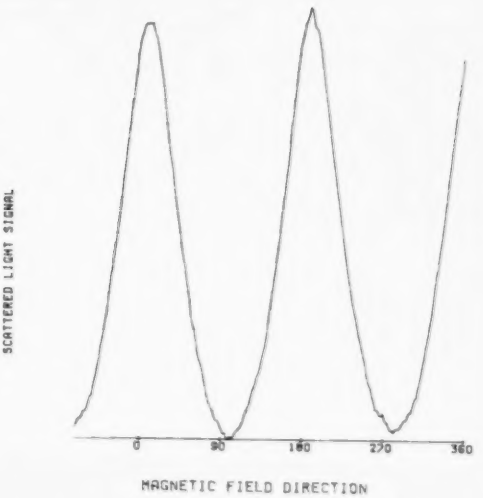

Figure 37. Chrysotile (Union Carbide)

SCATTERED LIGHT PROFILES

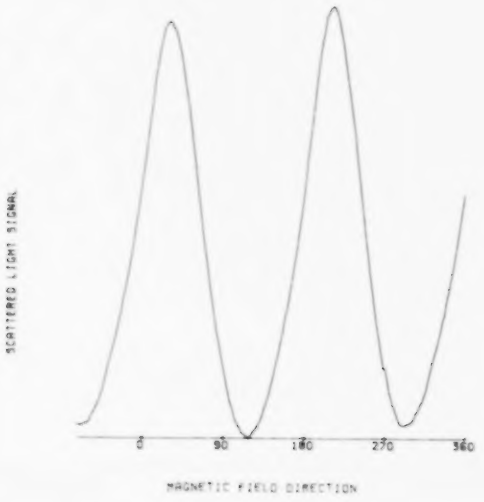

Figure 38. Lizardite
("Owens Pit", Ontario)

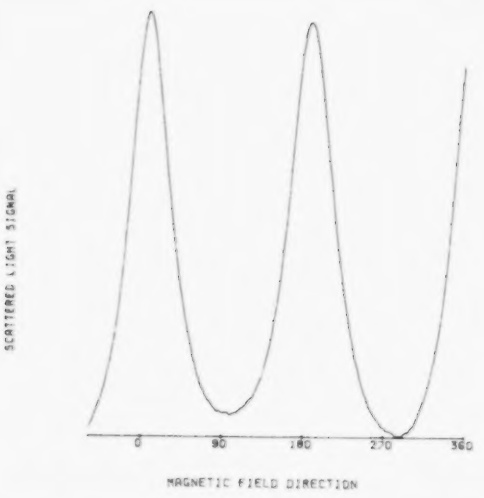

Figure 39. Picrolite
(Broughton, Quebec)

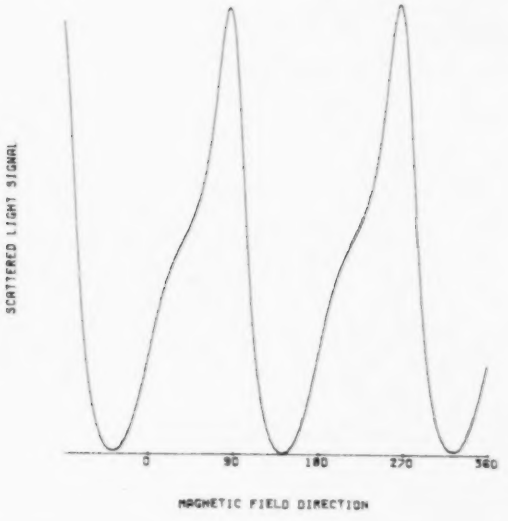

Figure 40. Antigorite
(East Broughton, Quebec)

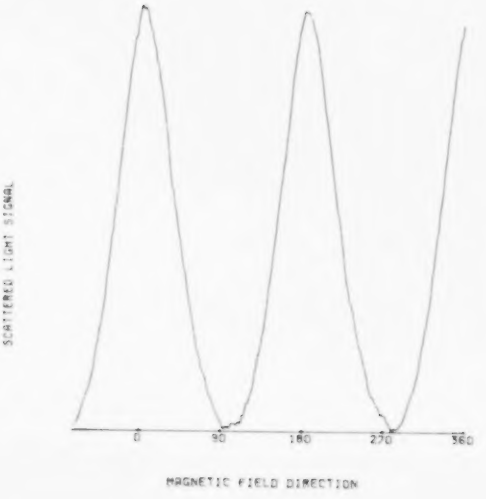

Figure 41. Talc
(Broughton, Quebec)

SCATTERED LIGHT PROFILES

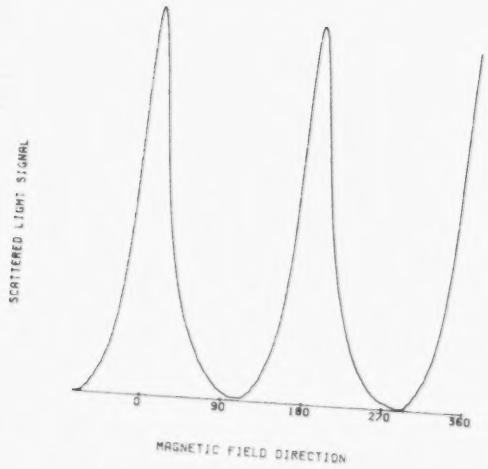

Figure 42. Nemalite
(Asbestos, Quebec)

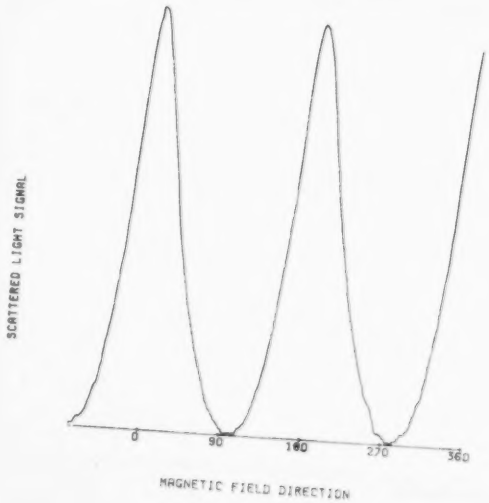

Figure 43. Brucite
(Asbestos, Quebec)

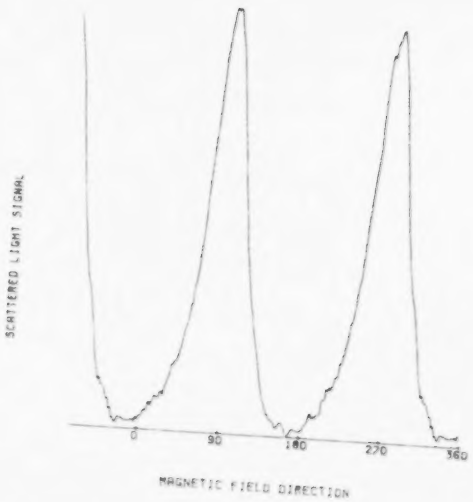

Figure 44. Tremolite
(Elzivir, Ontario)

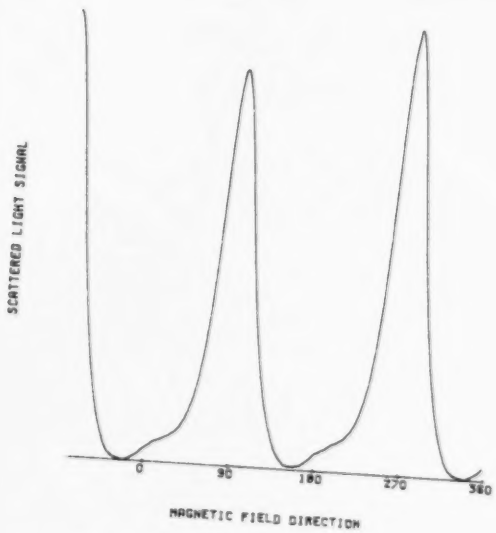

Figure 45. Tremolite
(Clarendon, Ontario)

SCATTERED LIGHT PROFILES

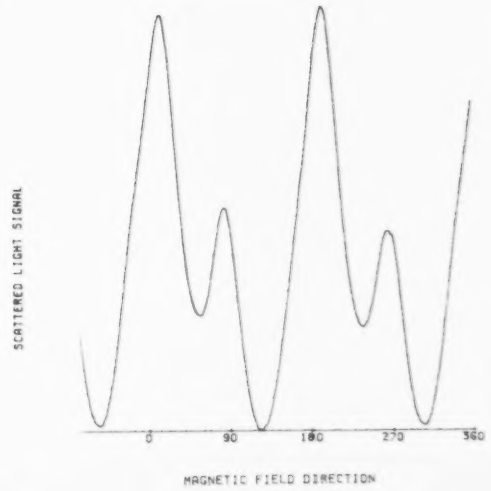

Figure 46. Tremolite (Arctic)

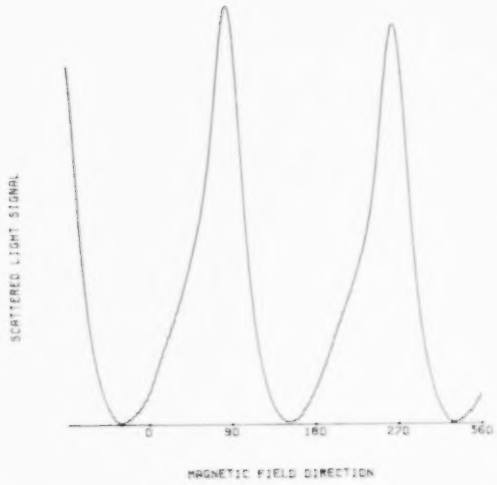

Figure 47. Tremolite (Inyo County, Cal.)

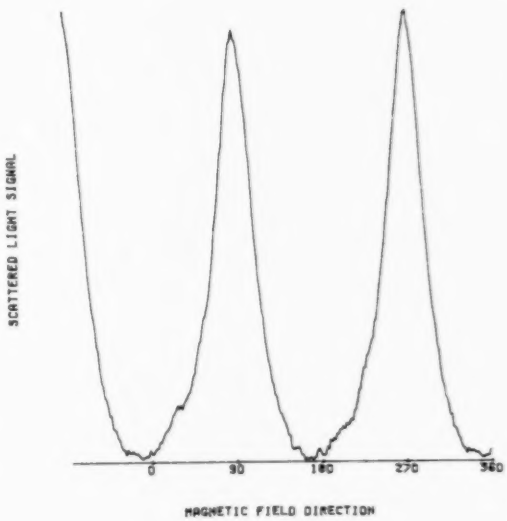

Figure 48. Tremolite (Transvaal, RSA)

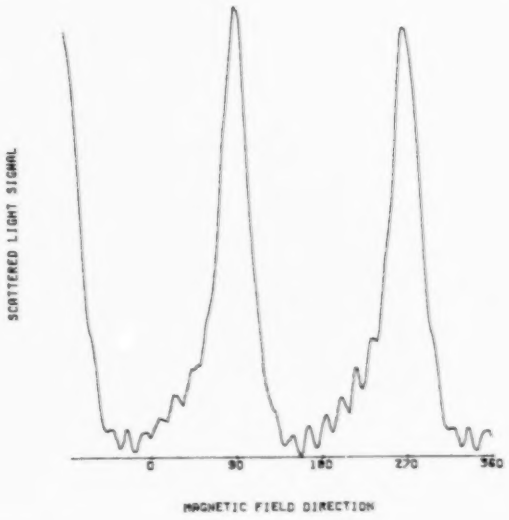

Figure 49. Tremolite (Yakutya, USSR)

SCATTERED LIGHT PROFILES

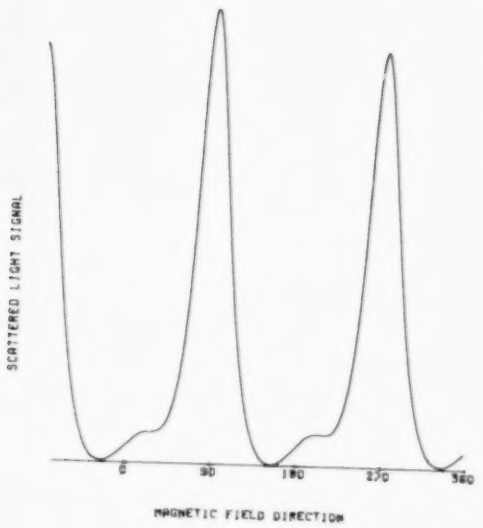

Figure 50. Actinolite (Marbridge, Quebec)

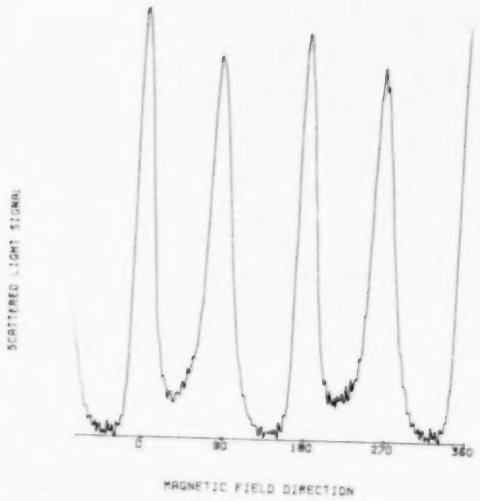

Figure 51. Amosite (UICC)

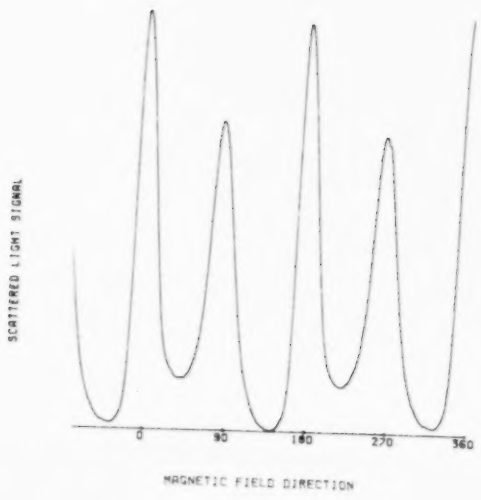

Figure 52. Amosite (Lyndberg, RSA)

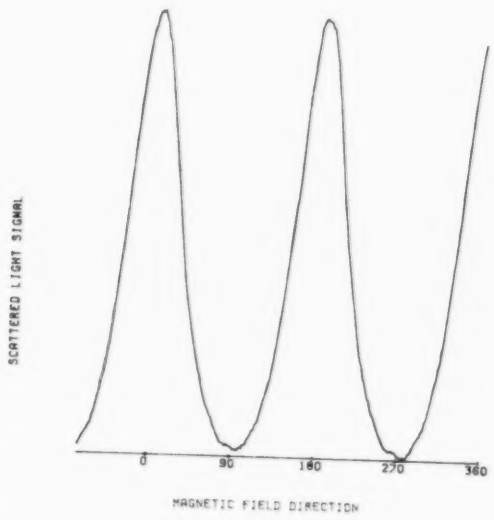

Figure 53. Cummingtonite (Soutpansberg, RSA)

SCATTERED LIGHT PROFILES

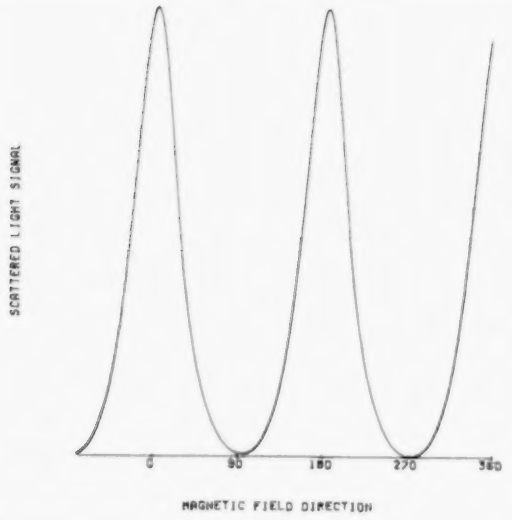

Figure 54. Cummingtonite
(Mikanui, New Zealand)

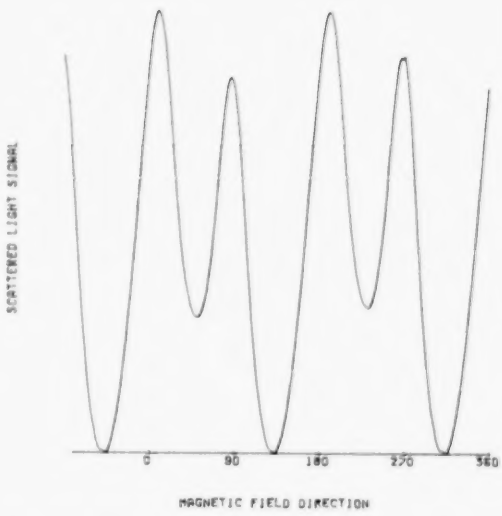

Figure 55. Cummingtonite
(Lead, South Dakota)

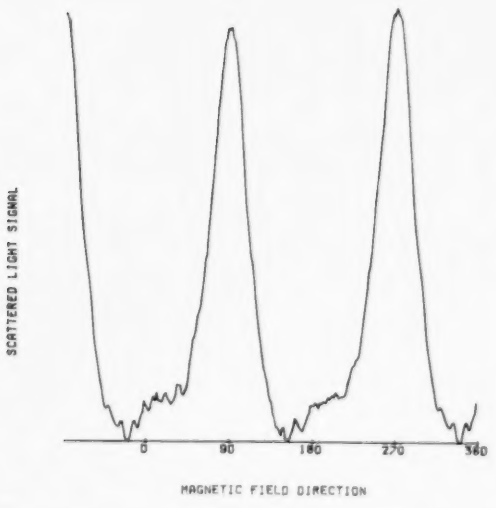

Figure 56. Grunerite
(Health Lake, Ontario)

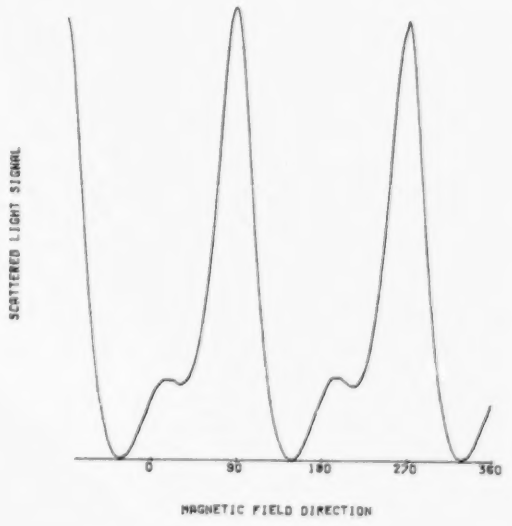

Figure 57. Grunerite
(Humbolt, Michigan)

SCATTERED LIGHT PROFILES

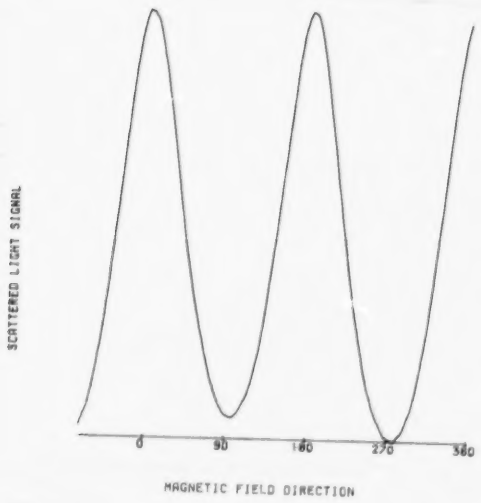

Figure 58. Minnesotaite
(Mesabi, Minnesota)

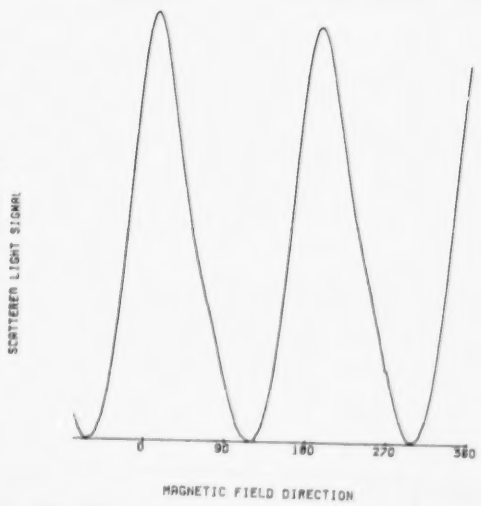

Figure 59. Stilpnomelane
(French Ridge, N.Z.)

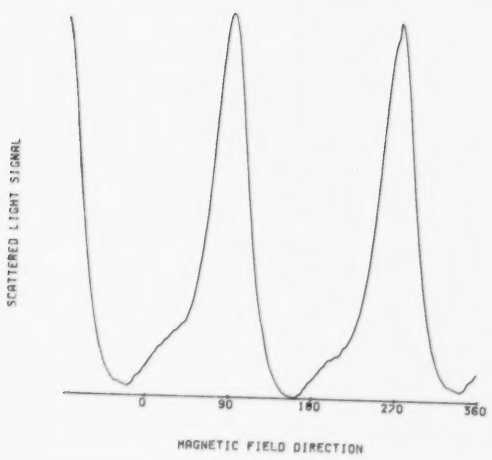

Figure 60. Hornblende
(Ross, Ontario)

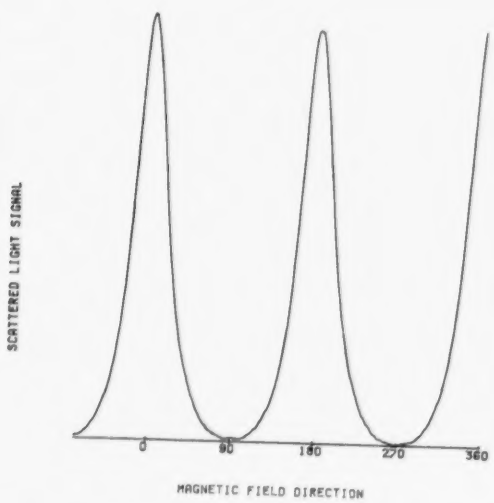

Figure 61. Suspected Omphacite
(Frontenac Co. Ont.)

SCATTERED LIGHT PROFILES

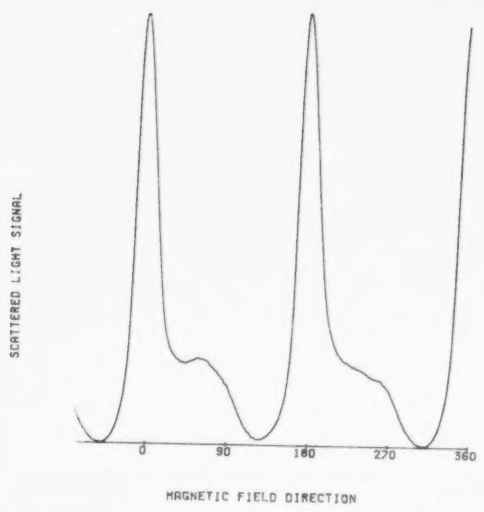

Figure 62. Crocidolite (UICC)

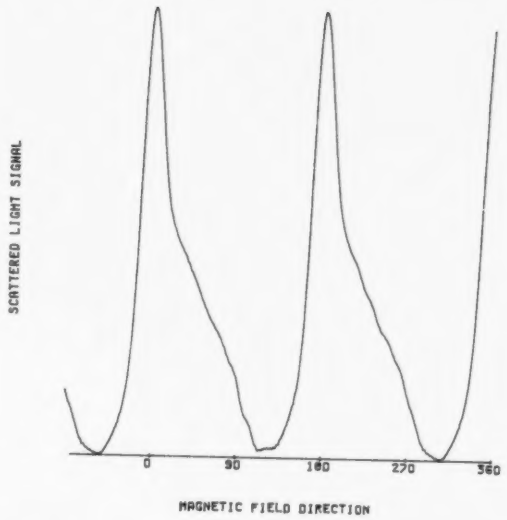

Figure 63. Crocidolite (Prieska, RSA)

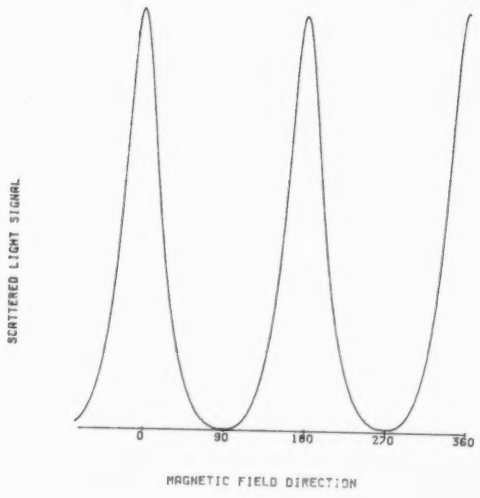

Figure 64. Riebeckite (St. Peter's Dome, Col.)

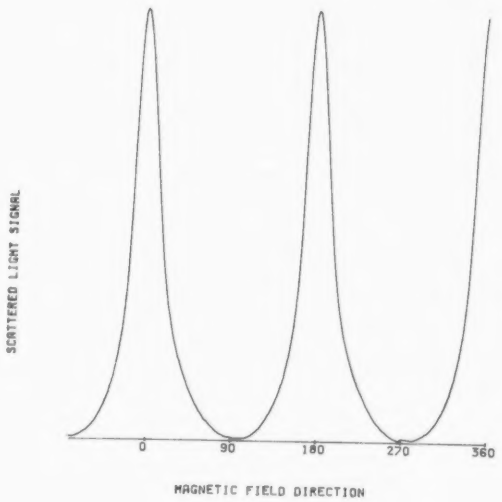

Figure 65. Anthophyllite (UICC)

SCATTERED LIGHT PROFILES

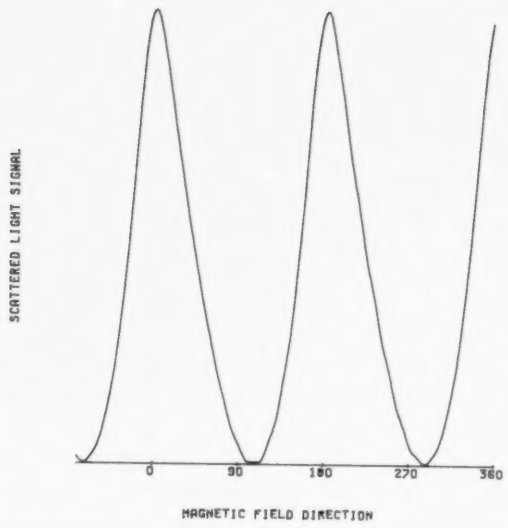

Figure 66. Anthophyllite (Montauban, Quebec)

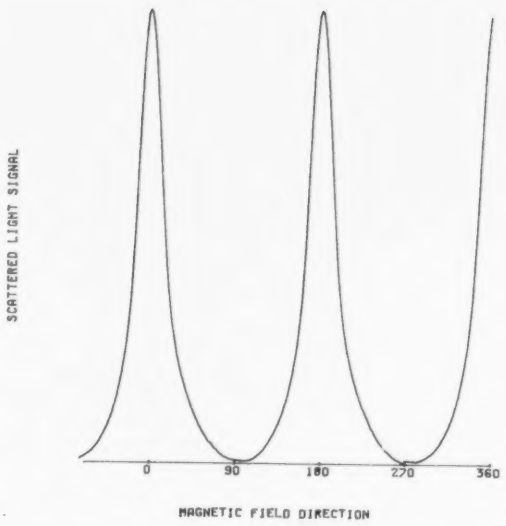

Figure 67. Anthophyllite (Salt Mountain, Georgia)

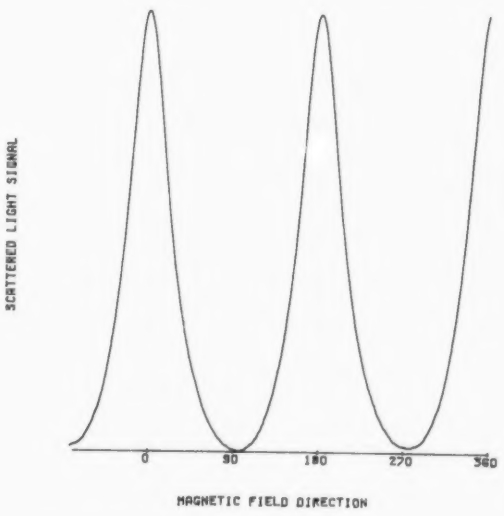

Figure 68. Gedrite (Telemark, Norway)

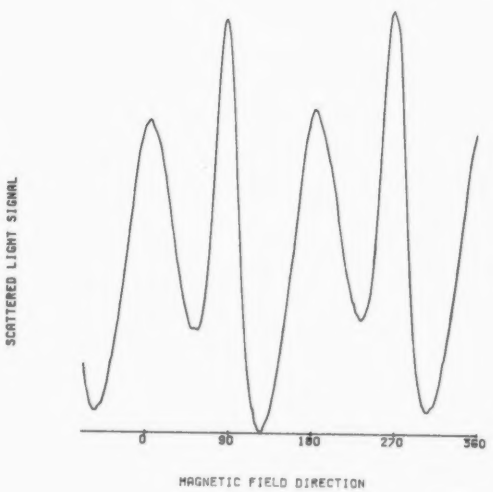

Figure 69. Howieite (Laytonville, Cal.)

SCATTERED LIGHT PROFILES

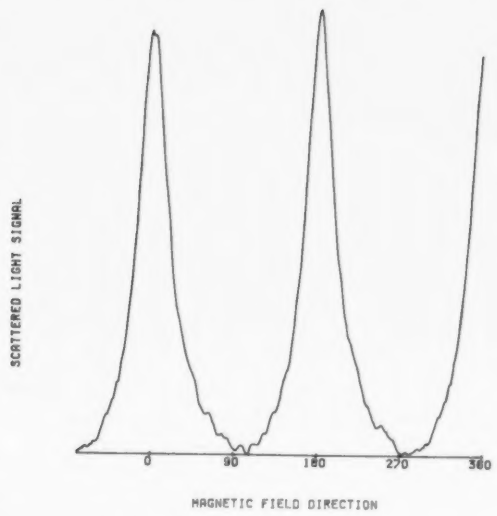

Figure 70. Wollastonite (Asbestos, Quebec)

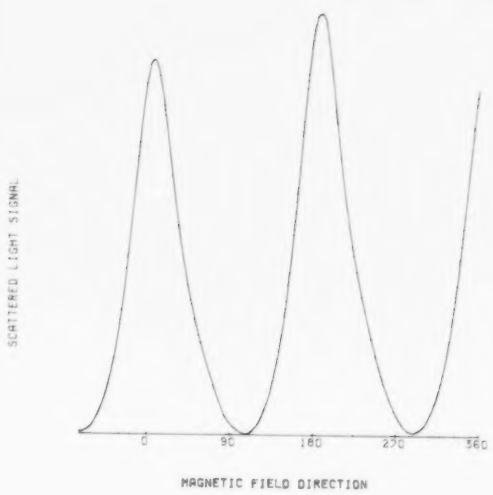

Figure 71. Wollastonite (Meldon, Quebec)

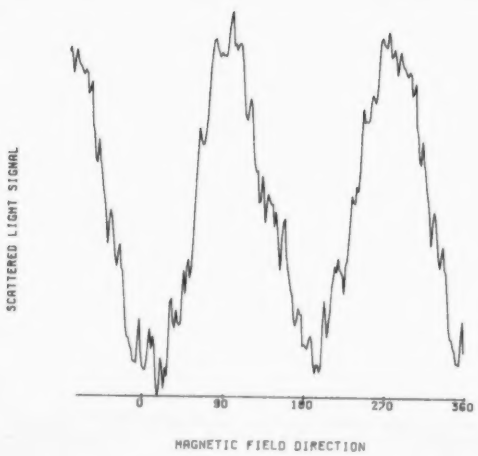

Figure 72. Halloysite (Eureka, Utah)

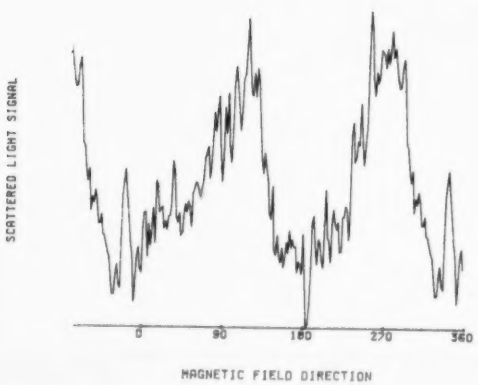

Figure 73. Halloysite (Delta, Utah)

SCATTERED LIGHT PROFILES

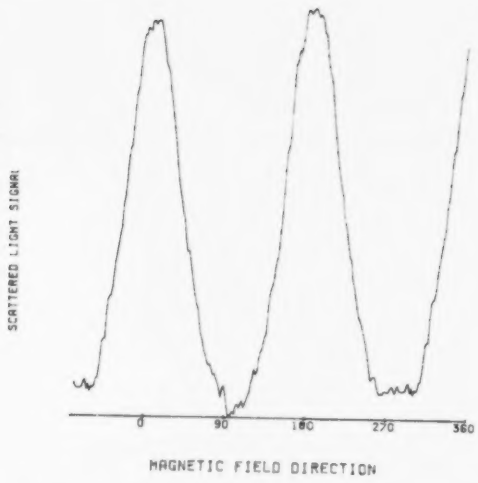

Figure 74. Palygorskite
(Metaline Falls, Wash.)

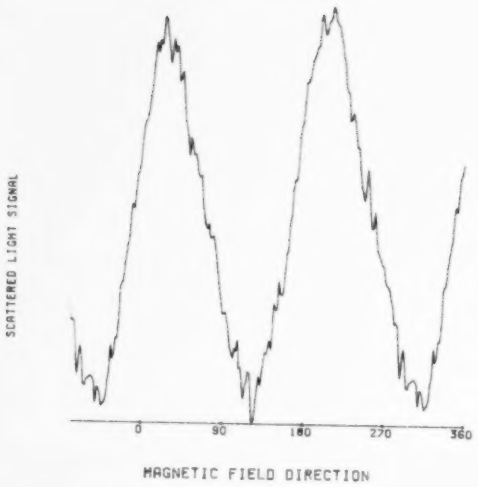

Figure 75. Palygorskite
(Pormona, Cal.)

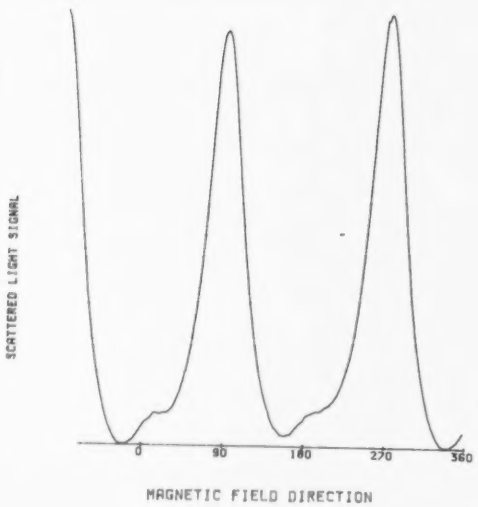

Figure 76. Xonotlite
(Asbestos, Quebec)

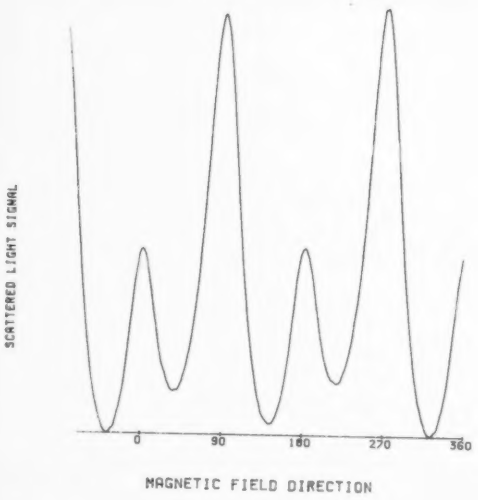

Figure 77. Xonotlite
(Wakefield, Quebec)

SCATTERED LIGHT PROFILES

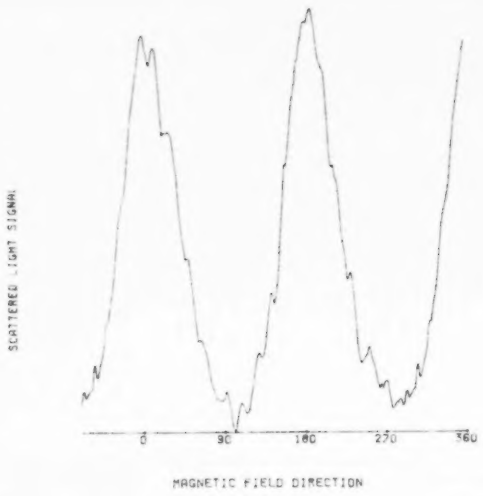

Figure 78. Phlogopite
(Phalaborwa, RSA)

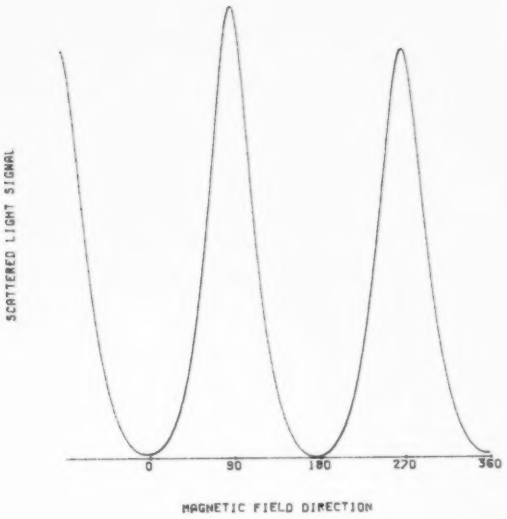

Figure 79. Pectolite
(Thetford, Quebec)

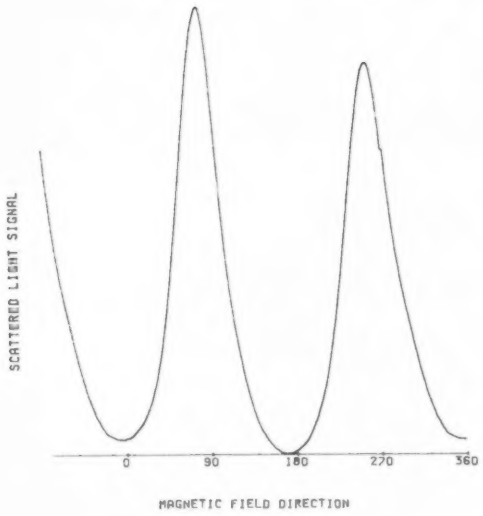

Figure 80. Pectolite
(Japan)

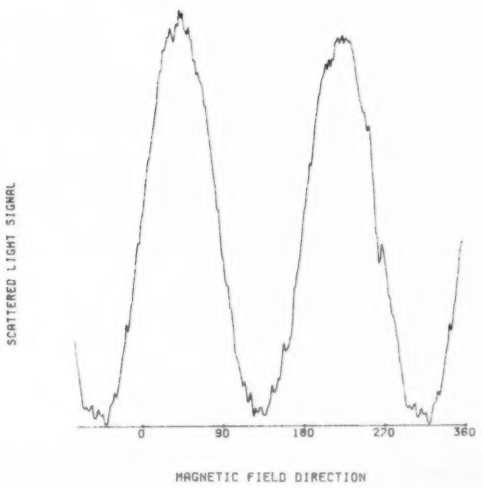

Figure 81. Diatomaceous Earth
(Seitz Supra EKS Filter)

SCATTERED LIGHT PROFILES

(c) Brucite and lizardite can be mistaken for chrysotile, since they both display broad P-peaks.

(d) All tremolite samples and the actinolite sample display sharp N-peaks only.

(e) Cummingtonite generally displays sharp P-peaks with the exception of the Mikanui sample which aligns at about 15° in the T-mode.

(f) The grunerite sample displays sharp N-peaks.

(g) The crocidolite samples display sharp P-peaks.

(h) Anthophyllite displays broad P-peaks similar to those of chrysotile.

(i) Wollastonite displays broad P-peaks similar to those of chrysotile.

(j) The amosite samples display sharp P-peaks and N-peaks.

It is evident that if the primary purpose is the detection of "asbestos" there is some potential for interference by fibrous species other than those normally considered as asbestos. Broad peaks also occur from platy minerals such as phlogopite; these are a consequence of the presence of cleavage fragments which have high aspect ratios. Assuming that the purpose of the technique is to determine if *any fibrous mineral species* are present, then it is highly successful, extremely sensitive, and allows some discrimination between species.

It was at first thought that general non-fibrous particulate would contribute only to the base-line level, and would not yield any peaks. As discussed in Section 5.3.3, this is not the case. The peaks at 45° and 225° from general particulate seriously overlap those at 0° and 180° from chrysotile, and may also embed the peaks from low concentrations of amphibole. Where there are large general particulate peaks, measurements of low fiber concentrations will be possible with the use of profile subtraction techniques. Where the general particulate level is too high for an effective measurement to be made, methods for specific concentration of fibers must be employed.

SECTION 7

METHODS FOR CONCENTRATION OF FIBERS

7.1 NON-SPECIFIC FIBER CONCENTRATION

Samples which on direct examination fail to yield any scattered light peaks at 0° and 180°, or at 90° and 270°,may have fiber concentrations below the detection limit of the equipment. In these cases non-specific fiber concentration may be applied to increase the actual fiber concentration to a value within the sensitive range. This can be achieved by filtration of a large volume of water and redispersal of the collected particulate in a smaller volume of double-distilled particle-free water. A Nuclepore capillary pore polycarbonate or polyester filter is used for this filtration, and the collected particulate is redispersed in a small plastic beaker of water by placing it in an ultrasonic bath for a few minutes. The filter is then removed and discarded, after which the concentrated dispersion can be examined using the light scattering equipment.

Along with concentration of the fibers, this simple procedure also concentrates the other particulate. The non-fibrous component of the particulate, particularly that which is affected by the magnetic field, may be of too high a concentration for a reliable measurement of the fiber content to be made. In this case specific fiber concentration methods must be employed.

7.2 REMOVAL OF ORGANIC PARTICLES

The ozone-ultraviolet oxidation procedure described elsewhere[17,18,19] is an effective means for removal of organic particles from drinking water supplies. Although some refractory organics are not affected, improvement in filtration rate always occurs after the treatment, which indicates that significant removal of organic particulate has been achieved. Essentially, 1% ozone gas is bubbled through the sample while it is irradiated by short wavelength ultraviolet light from a submerged lamp. Treatment for about 3 hours has been found adequate for most water samples; a noticeable reduction in turbidity is usually observed.

7.3 SPECIFIC CONCENTRATION OF CHRYSOTILE

The two-phase liquid separation (TPLS) technique[11] was originally thought to be directly applicable to specific concentration of chrysotile. However, although it was highly effective in separation of chrysotile from artificially-prepared dispersions, it produced no extraction of chrysotile from drinking water collected in Sherbrooke, Quebec. This

drinking water is known to contain 40 - 80 MFL of chrysotile, measured by electron microscopy. This technique, therefore, was not investigated further.

As part of the overall research program on analytical methods,[17] a discovery was made that chrysotile asbestos can be collected on the inside surfaces of unsterile plastic containers. Although the precise mechanism is not yet fully understood, it is known that the surface electrical charge of chrysotile causes some complex organic materials of high molecular weight to attach to its surface. These complex organic materials, probably polysaccharides, are secreted by some single cell biological organisms which seem always to be present in drinking water. When the plastic container is shaken in a reciprocal laboratory shaker, the organisms, along with scavenged chrysotile fibers, contact the internal surface of the container more frequently and become attached to it. Complete attachment of all chrysotile is obtained using this procedure on artificial dispersions of Union Carbide or UICC Canadian chrysotile in distilled, but unsterile, water. The most abundant organism in this water was a species of pseudomonas, at a concentration of about 10^7 viable organisms per liter. The technique is also effective in removal of chrysotile from Sherbrooke drinking water.

The attachment of chrysotile to the container walls is achieved to a maximum extent after the sample has been shaken at a frequency of about 2.5 cycles/second for a minimum of 48 hours. The liquid sample itself, which then contains only a small proportion of the original chrysotile and all of the other particulate, is discarded. The bottle is refilled using clean double-distilled water, and treated using the ozone-UV technique, which oxidizes the organic materials and releases the fibers from the container walls. The bottle is afterwards treated in an ultrasonic bath for about 15 minutes to ensure complete dispersal of the fibers. A suspension of suitable concentration of chrysotile for measurement in the light scattering system can then be prepared by the filtration technique described in 7.1.

The observation of this biological scavenging effect has serious implications for the sample preparation techniques normally used for measurements of fiber concentration by electron microscopy; a complete account of the studies has been described.[17,20]

The biological scavenging of asbestos fibers did not appear to be completely specific for chrysotile asbestos; crocidolite and amosite also displayed some separation, although studies of the separation of these amphibole types were not completed in view of the greater promise shown by magnetic separation techniques. Table 5 shows examples of the results obtained.

The recoveries for artificially-prepared dispersions in distilled water were usually close to 100%, and with very few fibers remaining in suspension after the shaking operation. For a naturally-occurring chrysotile dispersion from Sherbrooke, Quebec the recovery was about 45%, indicating either that some fundamental property of the fibers was

TABLE 5. SUMMARY OF FIBER REMOVAL FROM WATER SAMPLES

Sample	Concentration of Initial Suspension, MFL	Concentration of Fibers Remaining in Suspension, MFL	Concentration† of Fibers Separated from the Initial Suspension, MFL	Recovery Efficiency,* (Percent)
UICC Chrysotile in unsterile distilled water.	23.6	5.0	32.5	87
Union Carbide Chrysotile in unsterile distilled water.	78.4	< 0.5	64.5	99
Sherbrooke (Quebec) Municipal water	42	24	18	45
UICC Crocidolite in unsterile distilled water	32.3	0.7	24.5	97
UICC Crocidolite in unsterile distilled water	140	47	118	70
UICC Amosite in unsterile distilled water	Not Measured	2.0	12.1	85
Mississauga (Ontario) Drinking Water Spiked with Crocidolite	12.9	6.0	5.6	45

*The recovery efficiency was determined as the ratio of the concentration of separated fibers to the sum of the separated fibers and those remaining in suspension.

†Concentration expressed as a value referring to the volume of the initial suspension.

different or that the bacteria were in some way less efficient in their scavenging behavior. The same consideration applies to crocidolite added to a municipal drinking water, which was separated with a reduced efficiency of 45%.

Because of the simplicity of the technique, it is directly applicable to the rapid screening method. Further investigation of the effect is needed to develop it into a controlled procedure.

7.4 SPECIFIC CONCENTRATION OF AMPHIBOLES

Magnetic separation[21,22] of UICC amosite from aqueous suspensions was described by Timbrell.[23] The published data, however, are based on retention efficiencies measured by the magnetic alignment method, and do not indicate the numerical fiber retention efficiency, nor whether the separation is strongly size selective. As part of the investigation of concentration methods, the published design of magnetic separator was investigated using an aqueous suspension of UICC amosite. The apparatus used is shown in Figure 82; 0.5 grams of magnetic stainless steel wool with a wire diameter of 80 μm occupied 1.5 cm immediately above the outlet valve at the bottom of a 50 mL buret. The buret was arranged so that the steel wool was between the poles of a magnet. Each 10 mL aliquot of the amosite suspension was successively passed through the separator at a flow rate of about 2 mL/minute without attempting to remove the fibers retained from previous samples. The magnetic field was increased to a higher value for each successive aliquot, to the maximum field of 1.5 T. The filtrates were prepared for fiber counting in the TEM. Filtrations for the TEM samples were carried out in a magnetic field, so that separate measurements could be made for P-type and N-type fibers. The results are shown in Figures 83 and 84, in which the numerical retention efficiencies are shown as functions of magnetic field strength. The retention efficiencies for both fiber types are similar. The maximum retention efficiency, for both P- and N-fibers, occurred at a field strength above 1.0 T.

The observation that the retention efficiency showed a similar correlation with magnetic field strength for both P- and N-fibers shows that the retention is not an effect of fiber orientation. P-fibers are aligned in a horizontal plane by the magnetic field and pass through the steel wool in a direction normal to their lengths. Since N-fibers are aligned with their lengths normal to the field, their orientations relative to the direction of movement are random. If retention depended only on fiber orientation relative to direction of motion, then the retention efficiency for N-fibers would be substantially less than for P-fibers. The close similarity in retention efficiency for P- and N-fibers suggests that fiber entrapment is a result of magnetic attraction between fibers and the steel wool.

Figure 84 shows the cumulative fiber number retention efficiency of the separator as a function of both magnetic field and fiber length. It can be seen that the separator is most efficient at the highest magnetic field strengths, but that fields considerably higher than 1.5 T would be

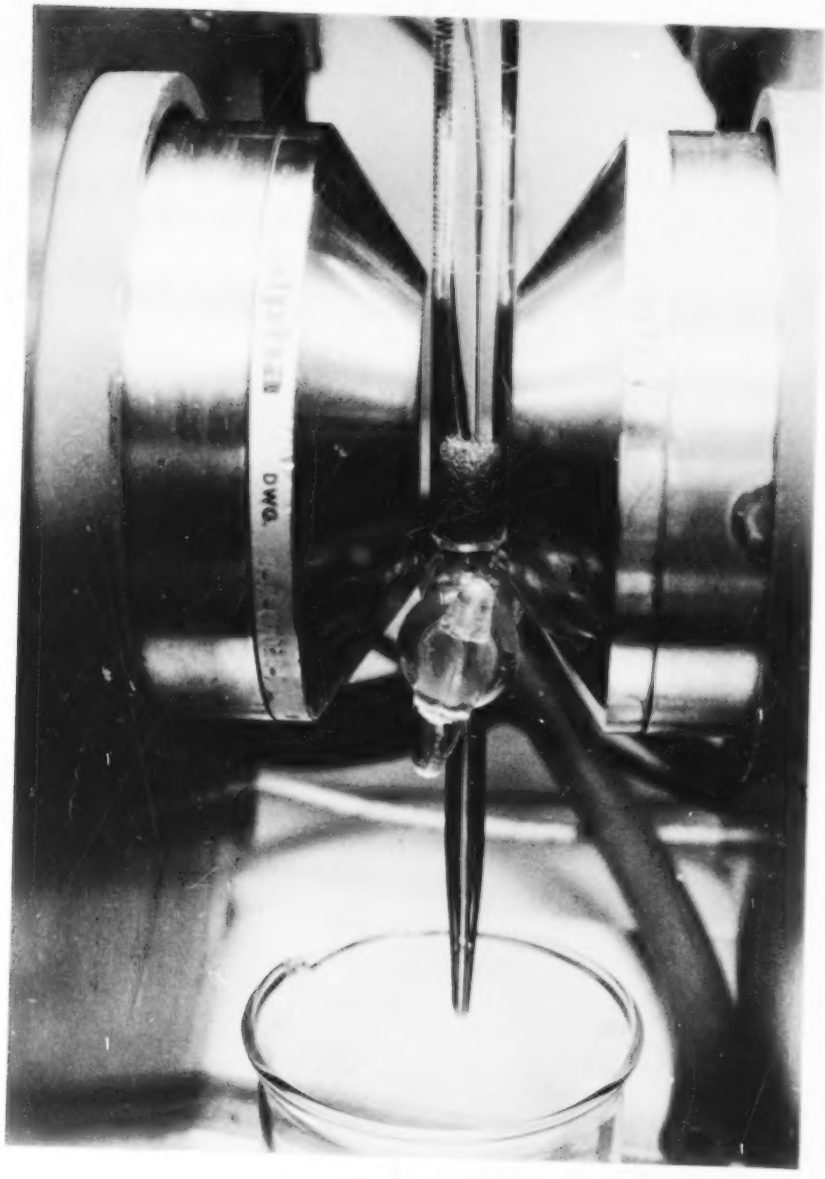

Figure 82. High gradient magnetic separator.

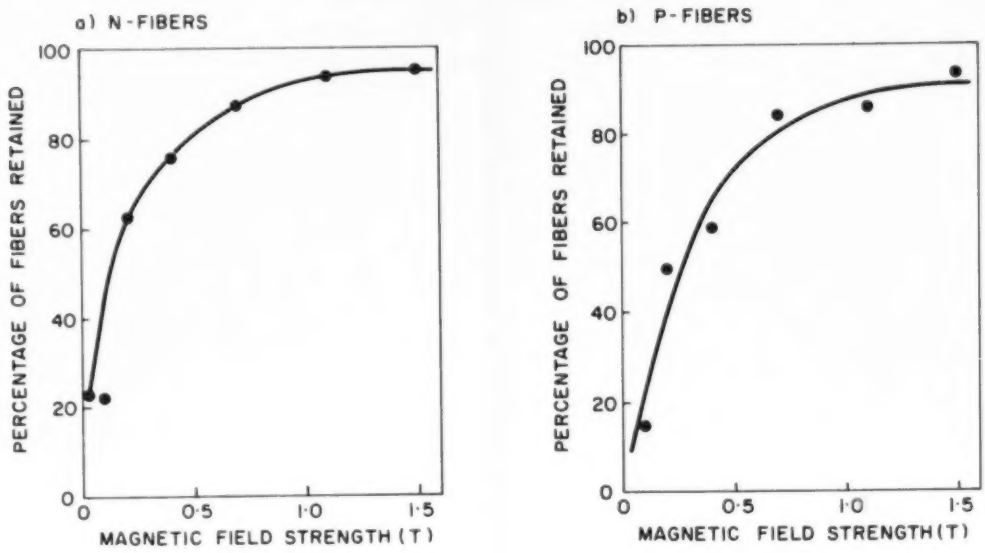

Figure 83. The effect of magnetic field strength on retention of amosite fibers; a) N-fibers and b) P-fibers.

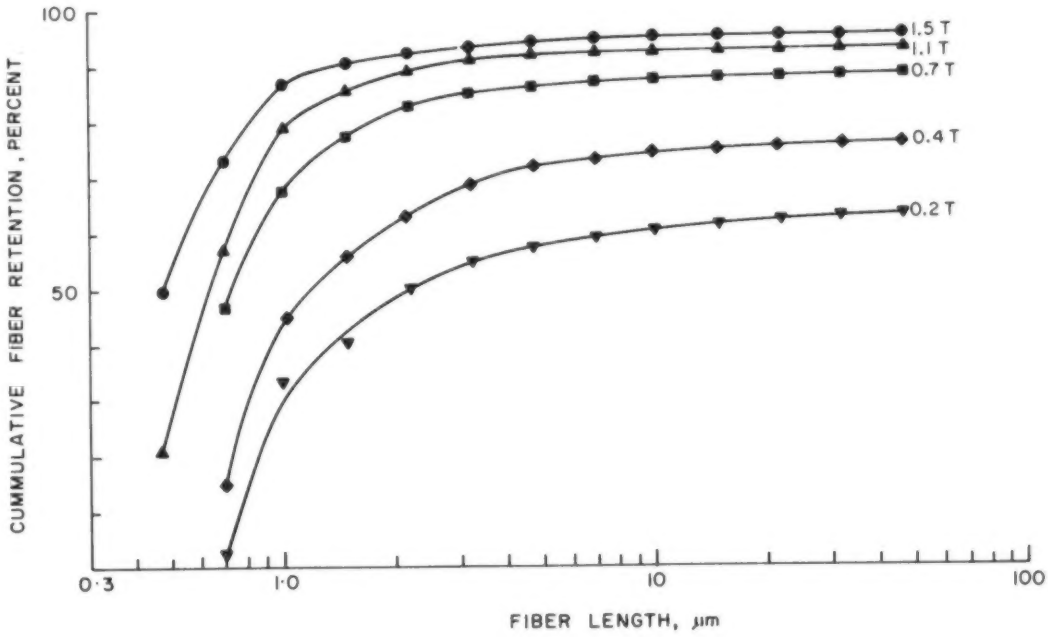

Figure 84. Magnetic separator retention efficiency for UICC amosite.

required to improve the performance significantly for fibers longer than about 1 μm. The efficiency for collection of fibers shorter than 1 μm falls very rapidly with fiber length. Nevertheless, in this configuration at a field of 1.5 T the cumulative efficiency still exceeds 50% for fibers shorter than 0.5 μm. At 1.5 T the efficiency of the separator in terms of mass is over 99.8%. This is a consequence of the fact that the larger fibers which comprise most of the mass are retained more efficiently.

Measurements using crocidolite dispersions indicate that the collection efficiency for crocidolite was very high in a magnetic field of 1.5 T. In these experiments, aliquots of a crocidolite dispersion were passed through the separator in a magnetic field of 1.5 T. The separator was then removed from the field, and 5 mL of distilled water were added. The collected fibers were redispersed by vigorous shaking, after which this washing procedure was repeated. The redispersed fiber suspensions, the filtrates, and samples of the original dispersion were then filtered in a magnetic field in order to prepare aligned fiber samples. The scattered light profiles for these samples were then obtained, and the results indicated that although the collection efficiency was high, the redispersal step yielded a recovery of only about 50%. It is possible that more complete removal could be obtained by the use of ultrasonic treatment.

Some studies have been performed using 400 mesh size electrolytically-etched nickel mesh as the magnetic separator element instead of the stainless steel wool. This shows promise as an element from which more complete removal of the collected fibers can be achieved without contamination from fragments of stainless steel. Collection efficiencies have not been measured systematically, but the initial results show that values comparable with those of the steel wool can be achieved. There is also considerable potential for further improvements in the design of magnetic separator elements for this application. It is important to recognize, however, that the separation is dependent on the iron content, and that the efficiency of collection of low-iron amphiboles such as tremolite may not be possible with simple systems such as that discussed.

SECTION 8

EVALUATION OF THE RAPID SCREENING TECHNIQUE: APPLICATION TO MUNICIPAL DRINKING WATER SAMPLES

The dynamic-fiber screening technique has been applied to the examination of three well-characterized municipal water samples. Beaver Bay, Minnesota drinking water is unfiltered Lake Superior water taken from a location about 10 miles south-west of Silver Bay. A sample of this water was ozone-UV treated to remove organics, and then agitated in the ultrasonic bath for about 15 minutes. The scattered light profile obtained directly and without concentration is shown as the solid curve in Figure 85. It can be seen that the peaks are asymmetric. This profile contains a component from the fibrous particulate superimposed on large general particulate peaks centered on angles of 45° and 225° to the magnetic field direction. A general particulate profile obtained from ground glass particles has been subtracted from the total profile, leaving an extracted profile which contains residual peaks at 0° and 180°, and at 90° and 270°. The extracted profile is plotted as the broken line. The two sets of peaks correspond to the known presence of cummingtonite-grunerite fibers at a concentration of about 17 MFL.

A sample from Sherbrooke, Quebec was examined, following the same method of specimen preparation. The scattered light profile obtained without further concentration is shown in Figure 86. Peaks occur in the profile, from which the general particulate contribution at 45° and 225° can be subtracted, leaving the chrysotile-type peaks at 0° and 180° in the extracted profile. This water contains about 40 MFL of chrysotile, as determined by TEM methods.

Drinking water in Mississauga, Ontario was last measured by TEM methods in 1977 and was found to contain less than about 2 MFL of chrysotile. The profile obtained for this water without any oxidation treatment is shown in Figure 87. The general particulate profile was subtracted, leaving an extracted profile containing only random instrumental noise. The profile is consistent with the known low fiber concentration, which is below the detection level of the equipment.

These three examples show the scattered light profiles obtained from measurement of municipal waters containing 17 MFL amphibole, 40 MFL chrysotile, and less than 2 MFL chrysotile respectively. It has been shown in Section 5.3.2 that the detection level for direct measurement of chrysotile is 5 MFL, and for amphibole is 0.5 MFL. In order to achieve the target detection level of 0.2 MFL for chrysotile, a pre-concentration by a factor of 25 is required; this can be achieved by either selective or non-selective pre-concentration. Amphibole fibers require pre-concentration by only a factor of 2.5 to achieve

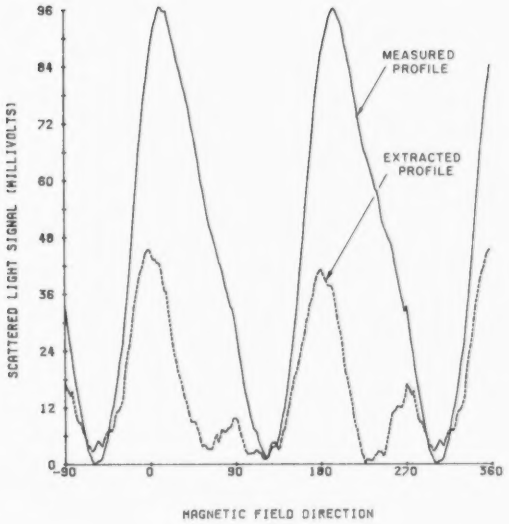

Figure 85. Scattered light profile of water sample from Beaver Bay, Minnesota, before and after subtraction of general particle peak.

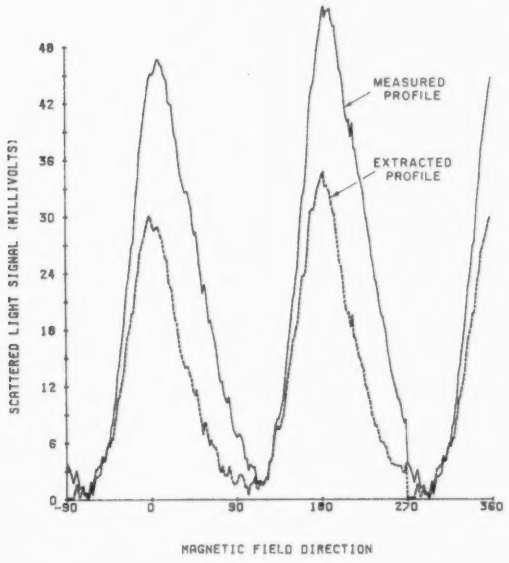

Figure 86. Scattered light profile of water sample from Sherbrooke, Quebec, before and after subtraction of general particle peak.

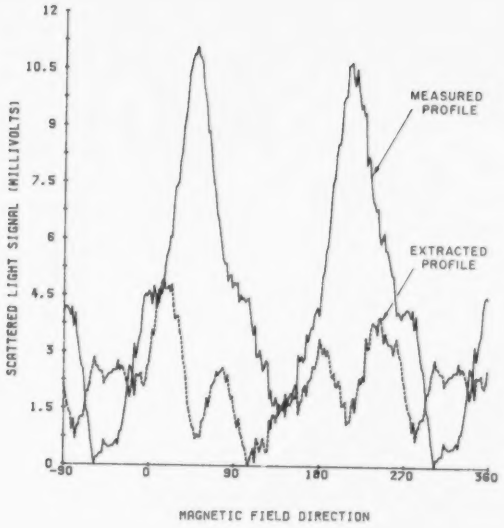

Figure 87. Scattered light profile of water sample from Mississauga, Ontario, before and after subtraction of general particle peak.

the target detection level and, depending on the iron content, this can be achieved by simple filtration and re-dispersal, or by the use of magnetic separation.

REFERENCES

1. Anderson, C.H. and Long, J.M. (1980) Interim Method for Determining Asbestos in Water. U.S. Environmental Protection Agency, Athens, Georgia. EPA-600/4-80-005, National Technical Information Service, Springfield, Virginia 22161.

2. Zielhuis, R.L. (editor) (1977) Public Health Risks of Exposure to Asbestos. Commission of the European Communities, Directorate-General for Social Affairs, Health and Safety Directorate, Pergamon Press Inc., Maxwell House, Fairview Park, Elmsford, New York 10523, U.S.A.

3. Barbeau, C. (1979) Evaluation of Chrysotile by Chemical Methods. In: Mineralogical Techniques of Asbestos Determination (R.L. Ledoux, ed.). Mineralogical Association of Canada, Department of Mineralogy, Royal Ontario Museum, 100 Queen's Park, Toronto, Ontario, Canada, M5S 2C6, p. 197-211.

4. Crable, J.V. (1966) Quantitative Determination of Chrysotile, Amosite and Crocidolite by X-ray Diffraction. Amer. Indust. Hygiene Assoc. J. 27, p. 293-298.

5. Crable, J.V. and Knott, M.S. (1966a) Application of X-ray Diffraction to the Determination of Chrysotile in Bulk or Settled Dust Samples. Amer. Indust. Hygiene Assoc. J. 27, p. 383-387.

6. Crable, J.V. and Knott, M.S. (1966b) Quantitative X-ray Diffraction Analysis of Crocidolite and Amosite in Bulk or Settled Dust Samples. Amer. Indust. Hygiene Assoc. J. 27, p. 449-453.

7. Ocella, E. and Maddalon, G. (1963) X-ray Diffraction Characteristics of Some Types of Asbestos in Relation to Different Techniques of Comminution. Medna. Lav., 54, p. 628-636.

8. Heidermanns, G. (1973) Asbestos Content Determination by Optical, Chemical, Radiographic and IR Spectographic Analysis Procedures. Staub (Engl.) 33, p. 67-72.

9. Birks, L.S., Fatemi, M., Gilfrich, J.V. and Johnson, E.T. (1975) Quantitative Analysis of Airborne Asbestos by X-ray Diffraction: Final Report on Feasibility Study, EPA-650/2-75-004. U.S. Environmental Protection Agency, National Environmental Research Center, Research Triangle Park, North Carolina, 27711.

10. Middleton, A.P. (1979) The Identification of Asbestos in Solid Materials. In: Asbestos Properties, Applications and Hazards, ed. Michaels, L. and Chissick, S.S. Published by John Wiley & Sons Ltd., New York, p. 260-277.

11. Melton, C.W., Anderson, S.J., Dye, C.F., Chase, W.E. and Heffelfinger, R.E. (1978) Development of a Rapid Analytical Method for Determining Asbestos in Water, EPA-600/4-78-066. U.S. Environmental Protection Agency, Environmental Research Laboratory, Athens, Georgia 30613.

12. Diehl, S.R., Smith, D.T. and Sydor, M. (1979) Optical Detection of Fiber Particles in Water, EPA-600/2-79-127. U.S. Environmental Protection Agency, Municipal Environmental Research Laboratory, Cincinnati, Ohio, 45268.

13. Timbrell, V. (1975) Alignment of Respirable Asbestos Fibres by Magnetic Fields. Annals of Occupational Hygiene, 18, p. 299-311.

14. Cressey, B.A. and Whittaker, E.J.W. (1980) Magnetic Orientation of Amphibole Fibres. Personal communication from B.A. Cressey.

15. Asbestos International Association (1979) Reference Method for the Determination of Airborne Asbestos Fibre Concentrations at Workplaces by Light Microscopy (Membrane Filter Method). Asbestos International Association, 68 Gloucester Place, London, W1H 3HL, England.

16. Ortiz, L.W. and Isom, B.L. (1974) Transfer Technique for Electron Microscopy of Membrane Filter Samples. American Indust. Hygiene Assoc. Journal 35 (No. 7), p. 423-425.

17. Chatfield, E.J., Stott, W.R. and Dillon, M.J. (1982) Development of Improved Analytical Techniques for Determination of Asbestos in Water Samples (Final Report). Contract No. 68-03-2717, S.E. Environmental Research Laboratory, U.S. Environmental Protection Agency, College Station Road, Athens, Georgia, 30613, U.S.A.

18. Chatfield, E.J. (1979) Preparation and Analysis of Particulate Samples by Electron Microscopy, with Special Reference to Asbestos. Scanning Electron Microscopy/1979/I, SEM Inc., AMF O'Hare, IL 60666, p. 563-578, 486.

19. Chatfield, E.J. (1978) A New Technique for Preparation of Beverage Samples for Asbestos Measurement by Electron Microscopy. Ninth International Congress on Electron Microscopy, Toronto, Vol. II, p. 102-103.

20. Chatfield, E.J. (1980) Analytical Procedures and Standardization for Asbestos Fiber Counting in Air, Water and Solid Samples. N.B.S. Special Publication 619, Proceedings of the NBS/EPA Asbestos Standards Workshop: Materials and Analytical Methods, National Bureau of Standards, Gaithersburg, Maryland, (Issued 1982), U.S. Government Printing Office, Washington, D.C. 20402, p. 91-107.

21. Oberteuffer, J.A. (1973) High Gradient Magnetic Separation, IEEE Transactions on Magnetics, 9, p. 303-306.

22. Oberteuffer, J.A. (1974) Magnetic Separation: A Review of Principles, Devices and Applications, IEEE Transactions on Magnetics, 10, p. 223-238.

23. Timbrell, V. (1977) Magnetic Separation of Respirable Asbestos Fibres, Filtration and Separation, 14, Number 3, p. 241-242.